

Thermodynamics of coherent interfaces under mechanical stresses. I.

Theory

T. Frolov^{1,*} and Y. Mishin^{1,†}

¹*Department of Physics and Astronomy, MSN 3F3,
George Mason University, Fairfax, Virginia 22030, USA*

Abstract

We present a thermodynamic theory of plane coherent solid-solid interfaces in multicomponent systems subject to non-hydrostatic mechanical stresses. The interstitial and substitutional chemical components are treated separately using chemical potentials and diffusion potentials, respectively. All interface excess quantities are derived using Cahn's (1979) generalized excess method without resorting to geometric dividing surfaces. We present expressions for the interface free energy as an excess quantity and derive a generalized adsorption equation and an interface Gibbs-Helmholtz equation which does not contain the interface entropy. The interface stress tensor emerges naturally from the generalized adsorption equation as an appropriate excess over bulk stresses and is shown to be generally non-unique. Another interface property emerging from the generalized adsorption equation is the interface excess shear. This property is specific to coherent interfaces and represents the thermodynamic variable conjugate to the shear stress applied parallel to the interface. The theory reveals a number of Maxwell relations describing cross-effects between thermal, chemical and mechanical responses of coherent interfaces. In Part II of this work this theory will be applied to atomistic computer simulations of grain boundaries.

PACS numbers: 64.10.+h, 64.70.K-, 68.35.-p, 68.35.Md

Keywords: interface thermodynamics, coherent interface, interface free energy, interface stress.

I. INTRODUCTION

Thermodynamics properties of interfaces can have a strong impact on microstructure development in materials by controlling phase nucleation, growth, coarsening and many other processes.^{1,2} The interface thermodynamics developed by Gibbs³ was formulated in terms of interface excesses relative to an imaginary geometric dividing surface separating the coexisting phases. Gibbs defined the interface free energy γ as the reversible work expended to create a unit area of the interface. He showed that, while other excess quantities generally depend on the choice of the dividing surface, γ is unique and thus a meaningful and measurable quantity. Gibbs' work was focused on interfaces in fluid systems, for which he derived the adsorption equation expressing the differential $d\gamma$ in terms of differentials of temperature and chemical potentials of the components present in the system.

Gibbs³ also discussed solid-fluid interfaces and pointed out that their interface area can change in two different ways: when a new area of the interface is formed at fixed thermodynamic states of the phases, and when the solid phase is elastically stretched parallel to the interface. The second process leads to the definition of the interface stress τ_{ij} , a tensor quantity whose components are generally different from γ and can be positive or negative.⁴ Using a thought experiment with a solid equilibrated with three different fluids, Gibbs demonstrated that chemical potential of a non-hydrostatically stressed solid is not well-defined.³ At the time, solid solutions were unknown and Gibbs considered only single-component solids. When introducing γ for solid-fluid interfaces, he specifically placed the dividing surface so that the interface excess of the solid component would vanish and there would be no need to talk about its chemical potential. As was recently pointed out,⁵ this approach would not work for a multicomponent solid.

Cahn⁶ proposed a more general form of the adsorption equation for hydrostatic systems by solving a system of Gibbs-Duhem equations for the bulk phases and for a layer containing the interface. By eliminating the Gibbsian construct of dividing surface, Cahn's method offers a greater freedom of choice of intensive variables in the adsorption equation. In particular, Cahn's formalism rigorously introduces the interface excess volume, a quantity which is by definition zero in Gibbs' thermodynamics. Cahn⁶ also proposed a Lagrangian (L) formulation of the Shuttleworth equation⁴ for phase boundaries, $\tau_{Lij} = \partial\gamma_L/\partial\varepsilon_{Lij}$, and pointed to the importance of computing the derivative with respect to the elastic strain ε_{Lij} along a phase coexistence path. For solid-fluid interfaces subject to non-hydrostatic mechanical stresses, τ_{ij} has been formulated as an interface excess

quantity^{7–10} and computed by atomistic methods for several crystallographic orientations.^{7,8,10,11}

In comparison with solid-fluid interfaces, thermodynamics of solid-solid interfaces is more challenging for at least two reasons. Firstly, such interfaces are capable of supporting shear stresses parallel to the interface plane. The interface response to such stresses depends on the degree of coherency and can vary from perfect sliding for fully incoherent interfaces to perfectly elastic response for fully coherent interfaces.^{12–15} The elastic response should obviously lead to additional terms in the adsorption equation, with coefficients representing what can be called “interface excess shears”. Such terms do not appear in existing formulations of interface thermodynamics.^{3,6} Secondly, because of the undefined chemical potentials in non-hydrostatically stressed solids, a different treatment is needed for the $-\Gamma_i d\mu_i$ terms appearing in the adsorption equation for fluid systems.³ In the analysis of equilibrium between bulk solid phases, this problem was circumvented by using chemical potentials for interstitial components but diffusion potentials for substitutional components.^{13–15} It will be shown below that the same approach can be transferred to interface thermodynamics.

Elastic response of coherent interfaces was also analyzed within mechanical theories of interfaces.^{16–18} In such theories, the interface is treated as a surface separating two elastic media subject to applied stresses. Mechanical equilibrium conditions have been derived and possible excess deformations and stresses at both plane and curved interfaces have been identified. By contrast to thermodynamic theories,^{12–15} the mechanical theories do not impose the chemical or phase equilibrium conditions between the adjoining media. As a result, the interface free energy γ cannot be defined as the work of interface formation, which blocks the route to the formulation of the adsorption equation.

In this paper we present a thermodynamic treatment of plane coherent solid-solid interfaces subject to mechanical stresses. Our analysis employs Cahn’s generalized excess method⁶ and the solid-solid equilibrium theory developed by Robin¹² and Larchè and Cahn.^{13–15} As the authors before us,^{3,12–15} we do not rely on *a priori* chosen thermodynamic potentials; instead, all equations are derived *directly* from the First and Second Laws of thermodynamics. It is only after the derivation is complete that some of the equations can be rewritten in simpler and/or more intuitive forms by introducing appropriate thermodynamic potentials. We start the paper by reviewing thermodynamics of a single solid phase (Section II) and then formulate the coherent phase equilibrium conditions (Section III) in a form which prepares us for the subsequent thermodynamic analysis of interfaces. Section IV is central to this paper. In it, we define the free energy γ of a coherent

interface, reformulate it as an excess of appropriate thermodynamics potentials, introduce a number of other interface excess quantities, and finally derive the generalized adsorption equation and the interface version of the Gibbs-Helmholtz equation. These equations identify and define the interface excess shear, a property specific to coherent interfaces and conjugate to the shear stress applied parallel to the interface. They also define the interface stress tensor as an excess quantity and demonstrate that it is not unique. We derive a number of Maxwell relations describing interesting cross-effects between different interface properties. In Section V we discuss how the proposed coherent interface theory can be applied to incoherent interfaces and grain boundaries. Finally, in Section VI we summarize our work and outline possible future developments.

II. THERMODYNAMICS OF A SOLID PHASE

A. The network solid

Our treatment of a solid phase is based on the concept of a network solid introduced by Robin¹² and Larchè and Cahn.^{13,14} We assume that the solid contains a penetrating network which is preserved inside the solid and can be created or destroyed only at its boundaries. The network serves three functions:

1. Enables a description of finite deformations of the solid¹⁹ by associating physical points with network sites (or their small groups).
2. Is capable of carrying mechanical loads, allowing the solid to reach mechanical equilibrium under non-hydrostatic conditions.
3. Provides a *conserved* set of sites, called substitutional, which are completely, or almost completely, occupied by atoms.³⁵ Accordingly, all chemical components can be divided into substitutional (residing on substitutional sites) and interstitial (otherwise).³⁶

In a crystalline solid, its lattice is formed by substitutional sites and satisfies all three network properties. Since our theory is intended primarily for applications to crystalline solids, we will adopt the terminology in which we refer to the network as “lattice” and to the network sites as “lattice sites”. It should be noted, however, that our results are of more general validity and do not require that the solid have a long-range atomic ordering. The theory should be equally applicable to non-periodic structures such as network glasses or network polymers.

B. Kinematics of deformation of a solid phase

We will analyze the general case of *finite* deformations of a solid using the concept of a reference state.¹⁹ The choice of the reference state is arbitrary, although it is often convenient to choose a stress-free state. We will use the same Cartesian coordinate system for both the reference and deformed states. For any physical point defined by coordinates x'_i ($i = 1, 2, 3$) in the reference state, its coordinates x_i in the deformed state are functions of the reference coordinates, $\mathbf{x} = \mathbf{x}(\mathbf{x}')$. Any infinitesimal vector dx_i connecting two physical points in the deformed state is related to the infinitesimal vector dx'_j connecting the same two physical points in the reference state by the linear transformation

$$dx_i = \sum_{j=1,2,3} F_{ij} dx'_j, \quad (1)$$

where tensor \mathbf{F} is the deformation gradient with components

$$F_{ij} = \frac{\partial x_i}{\partial x'_j}. \quad (2)$$

It is assumed that $J := \det \mathbf{F} \neq 0$ and thus the reference coordinates can be expressed as functions of the deformed ones, $\mathbf{x}' = \mathbf{x}'(\mathbf{x})$. The respective infinitesimal vectors are related by the inverse deformation gradient \mathbf{F}^{-1} ,

$$dx'_i = \sum_{j=1,2,3} F_{ij}^{-1} dx_j. \quad (3)$$

Only six components of \mathbf{F} are needed to completely describe all deformations (strains) of a solid. Without loss of generality, we will set all sub-diagonal components of \mathbf{F} to zero,

$$\mathbf{F} = \begin{pmatrix} F_{11} & F_{12} & F_{13} \\ 0 & F_{22} & F_{23} \\ 0 & 0 & F_{33} \end{pmatrix}, \quad (4)$$

with the Jacobian

$$J = F_{11}F_{22}F_{33}. \quad (5)$$

It can be shown that \mathbf{F}^{-1} also has an upper-triangular form with diagonal elements

$$F_{ii}^{-1} = 1/F_{ii}, \quad i = 1, 2, 3. \quad (6)$$

The upper-triangular form of \mathbf{F} implies that for any small volume element with the shape of a parallelepiped, its bottom and top faces remain normal to the x_3 axis. Furthermore, the edge of the parallelepiped which is initially parallel to the x_1 axis remains parallel to it during the deformation. Deformation of small volume element described by Eq. (4) is illustrated by a two-dimensional schematic in Fig. 1.

C. Thermodynamic description of a homogeneous solid phase

Consider a homogeneous multicomponent solid containing K substitutional and L interstitial chemical components in a state of thermodynamic equilibrium. The defining property of the substitutional components is that their atoms fill a conserved set of lattice sites. Vacancies, i.e. unoccupied substitutional sites, are neglected for the time being and will be discussed separately in Section VI. Thus, the total number N of substitutional atoms in any given reference region remains constant in all thermodynamic processes. Interstitial atoms occupy otherwise empty positions between the lattice sites and their number in any given reference region can vary. Diffusion of both substitutional and interstitial atoms is allowed as long as it preserves the substitutional sites.

Consider a homogeneous region of the solid containing a total of N substitutional and n interstitial atoms and obtained by elastic deformation of a homogeneous reference region of volume V' . Suppose the reference region, and thus V' and N , are fixed. Then the internal energy U of the region is a function of its entropy S , the amounts of individual chemical components N_k and n_l , and the deformation gradient \mathbf{F} :

$$U = U(S, N_1, \dots, N_K, n_1, \dots, n_L, \mathbf{F}) \quad (\text{Fixed } N). \quad (7)$$

Due to the imposed substitutional constraint $\sum_k N_k = N = \text{const}$, only $(K - 1)$ independent variations of N_k are possible. To implement this constraint, we can arbitrarily choose one of the substitutional components as the reference component and assume that each time we add to the solid an atom of a different substitutional component k , we simultaneously remove an atom of the reference component.^{13–15} Let us choose component 1 as the reference and treat the amounts of all other substitutional components as independent variables. The amounts of the interstitial components can be varied without constraints.

Consider a reversible variation of state of the solid, with a fixed reference region, when it

exchanges heat with its environment, changes its chemical composition, and performs mechanical work. The differential of energy of the region is given by^{13,14}

$$dU = TdS + \sum_{k=2}^K M_{k1} dN_k + \sum_{l=1}^L \mu_l dn_l + \sum_{i,j=1,2,3} V' P_{ij} dF_{ji}, \quad (8)$$

where T is temperature, μ_l are chemical potentials of the interstitial atoms and M_{k1} are $(K - 1)$ diffusion potentials of the substitutional atoms. According to Eq. (8), the diffusion potential M_{k1} is the energy change when an atom of the substitutional component k is replaced by an atom of the reference component 1 while keeping all other variables fixed:

$$M_{k1} = \frac{\partial U}{\partial N_k} - \frac{\partial U}{\partial N_1}, \quad k = 2, \dots, K. \quad (9)$$

In the last term in Eq. (8), \mathbf{P} is the first Piola-Kirchhoff stress tensor, which is generally not symmetrical and is related to the symmetrical Cauchy stress tensor $\boldsymbol{\sigma}$ by¹⁹

$$\mathbf{P} = J\mathbf{F}^{-1} \cdot \boldsymbol{\sigma} \quad (10)$$

(the dot denotes the inner product of tensors and vectors). Because \mathbf{F}^{-1} is a upper-triangular matrix, the components P_{31} , P_{32} and P_{33} are proportional to the respective components of $\boldsymbol{\sigma}$:

$$P_{3i} = F_{11}F_{22}\sigma_{3i} = (J/F_{33})\sigma_{3i}, \quad i = 1, 2, 3, \quad (11)$$

where we used Eqs. (4), (5) and (6).

In preparation for the analysis of interfaces in Section IV, we will rewrite the mechanical work term in Eq. (8) by separating the differentials dF_{11} , dF_{12} and dF_{22} from dF_{13} , dF_{23} and dF_{33} :

$$dU = TdS + \sum_{k=2}^K M_{k1} dN_k + \sum_{l=1}^L \mu_l dn_l + \sum_{i=1,2,3} V' F_{11} F_{22} \sigma_{3i} dF_{i3} + \sum_{i,j=1,2} V' P_{ij} dF_{ji}. \quad (12)$$

The $(K + L + 6)$ differentials in the right-hand side of this equation are independent and their number gives the total number of degrees of freedom of a homogeneous solid phase.

D. Relevant thermodynamic potentials

Various thermodynamic potentials can be derived from Eq. (12) by Legendre transformations. As will become clear later, the potential relevant to coherent interfaces is

$$\Phi_1 := U - TS - \sum_{k=2}^K M_{k1} N_k - \sum_{l=1}^L \mu_l n_l - \sum_{i=1,2,3} (V F_{i3}/F_{33}) \sigma_{3i}, \quad (13)$$

where subscript 1 indicates the reference substitutional component and $V = JV'$ is the physical (deformed) volume of the homogeneous solid. For a fixed reference volume (and thus N),

$$\Phi_1 = \Phi_1(T, M_{21}, \dots, M_{K1}, \mu_1, \dots, \mu_L, \sigma_{31}, \sigma_{32}, \sigma_{33}, F_{11}, F_{12}, F_{22}). \quad (14)$$

Using Eq. (12) we obtain

$$d\Phi_1 = -SdT - \sum_{k=2}^K N_k dM_{k1} - \sum_{l=1}^L n_l d\mu_l - \sum_{i=1,2,3} (V F_{i3}/F_{33}) d\sigma_{3i} + \sum_{i,j=1,2} V' Q_{ij} dF_{ji}, \quad (15)$$

where we denote

$$\mathbf{Q} := J\mathbf{F}^{-1} \cdot \left(\boldsymbol{\sigma} - \sum_{m=1,2,3} \frac{F_{m3}}{F_{33}} \sigma_{3m} \mathbf{I} \right) \quad (16)$$

($\mathbf{I} \equiv \delta_{ij}$ is the identity tensor). Although \mathbf{Q} is a 3×3 tensor, only its components Q_{11} , Q_{21} and Q_{22} appear in Eq. (15).

While the potential Φ_1 will prove to be useful in interface thermodynamics, its role in thermodynamics of a bulk phase is less obvious. Unless the state of stress is hydrostatic, this potential depends on the choice of the coordinate axes through the stress-strain variables $\sigma_{31}, \sigma_{32}, \sigma_{33}, F_{11}, F_{12}, F_{22}$. In addition, Φ_1 depends on the choice of the reference state of strain.

Eq. (13) defines Φ_1 for a homogeneous solid region containing a given number N of substitutional sites. We can also define an intensive potential ϕ_1 as Φ_1 per substitutional atom:

$$\phi_1 := \Phi_1/N = U/N - TS/N - \sum_{k=2}^K M_{k1} C_k - \sum_{l=1}^L \mu_l c_l - \sum_{i=1,2,3} (\Omega F_{i3}/F_{33}) \sigma_{3i}. \quad (17)$$

Here $C_k := N_k/N$ and $c_l := n_l/N$ are concentrations of substitutional and interstitial components per substitutional site, U/N , S/N and Ω are the energy, entropy and volume per substitutional site, respectively.

Similarly, we can introduce K different potentials Φ_m , and accordingly ϕ_m , by choosing other substitutional components m as the reference species:

$$\phi_m := \Phi_m/N = U/N - TS/N - \sum_{k=1}^K M_{km} C_k - \sum_{l=1}^L \mu_l c_l - \sum_{i=1,2,3} (\Omega F_{i3}/F_{33}) \sigma_{3i}. \quad (18)$$

Note that we have extended the summation with respect to k from 1 to K using the property $M_{kk} \equiv 0$. Combining Eq. (18) with known properties of diffusion potentials,^{13–15} namely $M_{ik} = -M_{ki}$ and $M_{ij} = M_{ik} + M_{kj}$, the following relationship between different ϕ -potentials can be derived:

$$\phi_m - \phi_n = M_{mn}, \quad m, n = 1, \dots, K. \quad (19)$$

It also follows that

$$\sum_{k=1}^K M_{km} C_k = \sum_{k=1}^K (\phi_k - \phi_m) C_k = \sum_{k=1}^K \phi_k C_k - \phi_m. \quad (20)$$

Using Eqs. (18) and (20), we obtain the following thermodynamic relation for a homogeneous non-hydrostatic solid phase:

$$U - TS - \sum_{i=1,2,3} (V F_{i3}/F_{33}) \sigma_{3i} = \sum_{k=1}^K \phi_k N_k + \sum_{l=1}^L \mu_l n_l. \quad (21)$$

This equation closely resembles Gibbs' equation $U - TS + pV = \sum_n \mu_n N_n$ for hydrostatic systems (p being external pressure),³ with ϕ_k playing the role of chemical potentials. When the solid is in a hydrostatic state of stress, $\sigma_{ij} = -\delta_{ij}p$, the left-hand side of Eq. (21) reduces to the Gibbs free energy $U - TS + pV$. Accordingly, ϕ_k become real chemical potentials of the substitutional components.

E. The Gibbs-Duhem equation

We can now derive a Gibbs-Duhem equation for a multicomponent non-hydrostatically stressed solid. To this end, we again consider a variation of state in which the solid region exchanges heat with its environment, performs mechanical work, and changes its chemical composition by switching chemical sorts of substitutional atoms (at fixed N) and changing the amounts of interstitial atoms. Differentiating Eq. (13) and using the relation $d\Phi_1 = Nd\phi_1$ and dU from Eq. (12), we obtain the following Gibbs-Duhem equation:

$$0 = -SdT - \sum_{k=2}^K N_k dM_{k1} - Nd\phi_1 - \sum_{l=1}^L n_l d\mu_l - \sum_{i=1,2,3} (VF_{i3}/F_{33}) d\sigma_{3i} + \sum_{i,j=1,2} V'Q_{ij}dF_{ji}. \quad (22)$$

Applying Eq. (19), this equation can be rewritten as

$$0 = -SdT - \sum_{k=1}^K N_k d\phi_k - \sum_{l=1}^L n_l d\mu_l - \sum_{i=1,2,3} (VF_{i3}/F_{33}) d\sigma_{3i} + \sum_{i,j=1,2} V'Q_{ij}dF_{ji}. \quad (23)$$

In the particular case of hydrostatic processes, $Q_{ij} \equiv 0$ while $\sum_{i=1,2,3} (VF_{i3}/F_{33}) d\sigma_{3i} = -Vdp$. In this case Eq. (23) reduces to the classical Gibbs-Duhem equation derived for fluids,³

$$0 = -SdT - \sum_{k=1}^{K+L} N_k d\mu_k + Vdp, \quad (24)$$

where μ_k are chemical potentials of chemical components and N_k are their amounts.

Eq. (23) is a relation between differentials of the intensive variables which characterize thermodynamic states of solids in equilibrium. By contrast to the standard Gibbs-Duhem equation (24), it contains non-hydrostatic variations.

III. COHERENT EQUILIBRIUM BETWEEN SOLID PHASES

A. Definition of coherency and coherent interface

We next discuss coherent equilibrium between two homogeneous solid phases whose thermodynamic properties were introduced in Section II. We assume that the two phases, which we refer to as α and β , contain the same K substitutional and L interstitial components and are separated by an infinitely large, plane coherent interface normal to the x_3 direction (Fig. 2). Our definition of phase coherency follows the works of Robin¹² and Larchè and Cahn.^{13–15} Namely, a coherent transformation of a region of phase α to a region of phase β is accomplished by deformation of the lattice without creation or destruction of lattice sites. Thus, a coherent transformation fully preserves the reference region of the phase. All chemical components are allowed to diffuse during the transformation as long as the lattice sites remain intact. A more detailed discussion of the concept of coherency and examples of coherent transformations can be found in Refs. 12–15.

If a coherent transformation occurs on one side of a plane selected inside a single-phase region, it produces a coherent interface between the old and new phases. Advancement of the transformation front occurs by interface migration. For coherent phases, there is a single network of lattice

sites penetrating through both phases and deformed during the interface motion. In other words, the two-phase system can be described as a deformation map of the same reference region as each of the phases. Due to the lattice continuity across the interface, sliding is prohibited and the two-phase system responds to applied shear stresses elastically. (This is in contrast to incoherent interfaces, which do not support static shear stresses and do not preserve the lattice sites during their motion.)

We will adopt the following kinematic description of coherent two-phase systems. The deformation gradients of the phases, \mathbf{F}^α and \mathbf{F}^β , are taken relative to the *same* reference state and have the upper-triangular forms,

$$\mathbf{F}^\alpha = \begin{pmatrix} F_{11} & F_{12} & F_{13}^\alpha \\ 0 & F_{22} & F_{23}^\alpha \\ 0 & 0 & F_{33}^\alpha \end{pmatrix}, \quad (25)$$

$$\mathbf{F}^\beta = \begin{pmatrix} F_{11} & F_{12} & F_{13}^\beta \\ 0 & F_{22} & F_{23}^\beta \\ 0 & 0 & F_{33}^\beta \end{pmatrix}, \quad (26)$$

where the superscripts indicate the phases. These forms ensure that the x_3 direction in both phases remains normal to the interface plane during all deformations. In addition, the lateral deformation components F_{11} , F_{12} and F_{22} are common to both phases, which is a necessary condition for the absence of sliding. Thus, the two deformation gradients differ only in the components F_{i3} . The differences between these components form a vector,

$$\mathbf{t} := (F_{13}^\beta - F_{13}^\alpha, F_{23}^\beta - F_{23}^\alpha, F_{33}^\beta - F_{33}^\alpha), \quad (27)$$

which we call the *transformation vector*. Its geometric meaning is illustrated by the two-dimensional schematic in Fig. 2(c).

B. Coherent phase equilibrium conditions

The conditions of coherent phase equilibrium were derived for a single-component system by Robin¹² and generalized to multicomponent systems containing both substitutional and interstitial atoms by Larchè and Cahn^{13,14} (see Voorhees and Johnson²⁰ for review). The equilibrium conditions can be summarized as follows:

- (i) Temperature is uniform throughout the system.
- (ii) Diffusion potentials M_{k1} of all substitutional components and chemical potentials μ_l of all interstitial components are uniform throughout the system.
- (iii) The internal mechanical equilibrium condition, $\nabla' \cdot \mathbf{P} = 0$, is satisfied inside each phase (the divergence is taken with respect to the reference coordinates).
- (iv) The traction vector is continuous across the interface,

$$\mathbf{n}'^\alpha \cdot \mathbf{P}^\alpha = -\mathbf{n}'^\beta \cdot \mathbf{P}^\beta, \quad (28)$$

where vectors \mathbf{n}'^α and $\mathbf{n}'^\beta = -\mathbf{n}'^\alpha$ are unit normals to the phases in the reference state.³⁷ This condition reflects the continuity of the displacement vector across the interface. From Eqs. (28) and (11) it follows that the Cauchy stress components σ_{31} , σ_{32} and σ_{33} are also continuous across the interface.

(v) Finally, the so-called phase-change equilibrium condition^{13,14} must be satisfied. This condition expresses equilibrium with respect to virtual displacements of the interface in which a layer of one phase reversibly transforms to a layer of the other. Rewritten in our notations, the phase change equilibrium condition derived by Larchè and Cahn^{13,14} reads

$$\begin{aligned} U^\alpha - TS^\alpha - \sum_{k=2}^K M_{k1} N_k^\alpha - \sum_{l=1}^L \mu_l n_l^\alpha - \sum_{i=1,2,3} (V F_{i3}/F_{33})^\alpha \sigma_{3i} = \\ = U^\beta - TS^\beta - \sum_{k=2}^K M_{k1} N_k^\beta - \sum_{l=1}^L \mu_l n_l^\beta - \sum_{i=1,2,3} (V F_{i3}/F_{33})^\beta \sigma_{3i}. \end{aligned} \quad (29)$$

Here U , S , V are the energy, entropy and volume of the phases obtained by deformation of the same reference region. The total number of substitutional atoms is equal in both phases, $N^\alpha = N^\beta$, whereas the total number of interstitial components can be different ($n^\alpha \neq n^\beta$).

The equilibrium conditions (i)-(iii) are common to all types of interfaces. The differences between the coherent, incoherent and other types of interfaces lie in the remaining conditions (iv) and (v).

C. Derivation of the phase-change equilibrium condition

The phase-change equilibrium condition (29) was obtained from equation (41) of Larchè and Cahn¹⁴ by inserting our upper-triangular deformation gradients (25) and (26) and the interface normal $\mathbf{n} = (0, 0, 1)$. Note that Eq. (29) contains the terms $\left(V^\beta F_{13}^\beta / F_{33}^\beta - V^\alpha F_{13}^\alpha / F_{33}^\alpha \right) \sigma_{31}$ and

$\left(V^\beta F_{23}^\beta/F_{33}^\beta - V^\alpha F_{23}^\alpha/F_{33}^\alpha\right) \sigma_{32}$ proportional to the shear stresses σ_{31} and σ_{32} . These terms are specific to coherent interfaces and vanish for incoherent, solid-fluid and fluid-fluid systems which do not support such stresses. To elucidate the meaning of these terms and set the stage for the analysis of interface thermodynamics, we will present an alternate derivation of Eq. (29) which assumes that the equilibrium conditions (i) through (iv) are already satisfied.

At fixed values of the intensive variables $T, M_{21}, \dots, M_{K1}, \mu_1, \dots, \mu_L, \sigma_{31}, \sigma_{32}, \sigma_{33}, F_{11}, F_{12}, F_{22}$,³⁸ equilibrium between the phases is neutral, i.e., the interface can reversibly migrate up and down without altering thermodynamic states of the bulk phases. The phase change equilibrium condition expresses the neutrality of this equilibrium with respect to interface displacements. Consider a homogeneous layer of phase α parallel to the interface and containing a total of N substitutional atoms. Suppose the interface traveling down passes through this layer and transforms it completely to a layer of phase β . The initial and transformed states of the layer are shown schematically in Fig. 2(a,b). In both states, the layer contains the same total number of substitutional atoms, whereas the total number of interstitial atoms can be different.

Let us compute the change in internal energy of this layer. Because the transformation is reversible, this change depends only on the initial and final states (i.e., homogeneous phases α and β) and not on the transformation path. As the interface traverses the layer, it creates intermediate states that are not homogeneous. Instead of examining this actual transformation process, we will consider another, imaginary path on which the transformation occurs by homogeneous deformation of the layer with a simultaneous change in its chemical composition. Since the layer remains homogeneous during this process, its energy change can be obtained by integrating Eq. (12) derived previously for homogeneous variations. Remembering that the intensive parameters are fixed, the integration gives

$$U^\beta - U^\alpha = T(S^\beta - S^\alpha) + \sum_{k=2}^K M_{k1} (N_k^\beta - N_k^\alpha) + \sum_{l=1}^L \mu_l (n_l^\beta - n_l^\alpha) + \sum_{i=1,2,3} \left(V^\beta F_{i3}^\beta/F_{33}^\beta - V^\alpha F_{i3}^\alpha/F_{33}^\alpha\right) \sigma_{3i}. \quad (30)$$

The last term in Eq. (12) does not contribute to this equation because F_{11} , F_{12} and F_{22} are not varied. Eq. (30) recovers the phase-change equilibrium condition (29).

This derivation emphasizes that the last term in Eq. (30) represents the mechanical work, W_m , done by the stress components σ_{3i} during the phase transformation. This work term can be rewrit-

ten as

$$W_m = \sum_{i=1,2,3} F_{11} F_{22} V' \left(F_{i3}^\beta - F_{i3}^\alpha \right) \sigma_{3i} = F_{11} F_{22} V' \boldsymbol{\sigma} \cdot \mathbf{t}, \quad (31)$$

where \mathbf{t} is the transformation vector defined by Eq. (27) and illustrated in Fig. 2(c). It is important to note that, while $V^\alpha F_{i3}^\alpha / F_{33}^\alpha$ and $V^\beta F_{i3}^\beta / F_{33}^\beta$ individually depend on the choice of the reference state of strain, vector \mathbf{t} is an invariant and in principle measurable quantity characterizing the geometry of the transformation.³⁹ For incoherent and other interfaces incapable of supporting static shear stresses, W_m reduces to $F_{11} F_{22} V' \sigma_{33} t_3 = (V^\beta - V^\alpha) \sigma_{33}$. For coherent interfaces, additional work is done by the shear stresses along the components of \mathbf{t} projected on the interface plane.

Using the thermodynamic potential ϕ_1 defined by Eq. (17), the phase-change equilibrium condition (29) can be formulated as simply $\phi_1^\alpha = \phi_1^\beta$. Furthermore, by choosing other substitutional components as reference species, the following K relations can be obtained:

$$\phi_m^\alpha = \phi_m^\beta := \phi_m, \quad m = 1, \dots, K. \quad (32)$$

Thus, in a system with K substitutional chemical components, there are K potentials that have the same value in coexisting phases. This result resembles Gibbs' condition of equilibrium between fluid phases,³ with ϕ_m playing the role of chemical potentials.

D. The equation of coherent phase coexistence in the parameter space

The Gibbs-Duhem equation (22) establishes a relation between the differentials of $(K + L + 7)$ intensive parameters characterizing a single-phase solid under stress. When two solid phases coexist, their equilibrium imposes an additional constraint on possible variations of state of the phases. This constraint can be formulated by writing down the Gibbs-Duhem equation for each phase in terms of the same set of intensive parameters and requiring that the two equations hold simultaneously:

$$\begin{aligned} 0 = & -S^\alpha dT - \sum_{k=2}^K N_k^\alpha dM_{k1} - N^\alpha d\phi_1 - \sum_{l=1}^L n_l^\alpha d\mu_l \\ & - \sum_{i=1,2,3} (V^\alpha F_{i3}^\alpha / F_{33}^\alpha) d\sigma_{3i} + \sum_{i,j=1,2} V'^\alpha Q_{ij}^\alpha dF_{ji}, \end{aligned} \quad (33)$$

$$\begin{aligned}
0 = & -S^\beta dT - \sum_{k=2}^K N_k^\beta dM_{k1} - N^\beta d\phi_1 - \sum_{l=1}^L n_l^\beta d\mu_l \\
& - \sum_{i=1,2,3} \left(V^\beta F_{i3}^\beta / F_{33}^\beta \right) d\sigma_{3i} + \sum_{i,j=1,2} V'^\beta Q_{ij}^\beta dF_{ji}.
\end{aligned} \tag{34}$$

Note that these equations are written for arbitrarily chosen amounts of the phases, i.e. generally $N^\alpha \neq N^\beta$. They can be combined into one equation by eliminating one of the differentials. This elimination leads to the equation

$$\begin{aligned}
0 = & -\{S\}_X dT - \sum_{k=2}^K \{N_k\}_X dM_{k1} - \{N\}_X d\phi_1 - \sum_{l=1}^L \{n_l\}_X d\mu_l \\
& - \sum_{i=1,2,3} \{V F_{i3} / F_{33}\}_X d\sigma_{3i} + \sum_{i,j=1,2} \{V' Q_{ij}\}_X dF_{ji},
\end{aligned} \tag{35}$$

where X is one of the extensive properties S , N_k ($k = 2, \dots, K$), N , n_l ($l = 1, \dots, L$), $V F_{i3} / F_{33}$ ($i = 1, 2, 3$) or $V' Q_{ij}$ ($i, j = 1, 2$). The curly braces are defined by

$$\{Z\}_X := Z^\alpha - Z^\beta X^\alpha / X^\beta \tag{36}$$

for any pair of extensive properties Z and X . The physical meaning of $\{Z\}_X$ is the difference between the property Z of the two phases when they contain the same amount of X . For example, $\{S\}_N$ is the difference between entropies of two homogeneous regions of the phases containing the same total number of substitutional atoms.

For any choice of X out of the above list, the respective differential coefficient in Eq. (35) vanishes because $\{X\}_X = 0$. The remaining $(K + L + 6)$ terms form a differential equation defining the coherent phase coexistence hypersurface in the configuration space of intensive parameters. Thus, a system of two coexisting coherent phases is capable of $(K + L + 5)$ independent variations, which is one degree of freedom less than for each phase taken separately. Knowing one equilibrium state of the two-phase system, all other states can be found by integrating Eq. (35) along different paths on the phase coexistence hypersurface.

Eq. (35) is an important result of this paper. It provides the phase rule for equilibrium between coherent phases and offers flexibility in choosing the independent variables corresponding to the available degrees of freedom through the choice of X . It generalizes the equation of phase coexistence derived by Gibbs for solid-fluid interfaces³ by incorporating shears parallel to the interface. Such shears are represented by the additional terms $\{V F_{i3} / F_{33}\}_X d\sigma_{3i}$ with $i = 1, 2$. To further elucidate the physical meaning of these terms, consider coherent equilibrium between two binary

substitutional solid solutions. For variations of the shear stress at a constant temperature and fixed lateral dimensions of the system,

$$\frac{dM_{21}}{d\sigma_{3i}} = -\frac{\{VF_{i3}/F_{33}\}_N}{\{N_k\}_N}, \quad (37)$$

where we chose $X = N$. This relation predicts that to maintain the equilibrium, variations in the diffusion potential in response to variations in the shear stress must be proportional to the transformation shear and inversely proportional to the difference between the phase compositions. In other words, this relation describes changes in the phase compositions caused by applied shear stresses.

It should be emphasized that Eq. (35) has been derived under the assumption of interface coherency. One might think that the phase coexistence equation for incoherent interfaces could be obtained as simply a particular case of Eq. (35) when σ_{31} and σ_{32} are zero. This is not so. In the absence of coherency, the lateral deformations of the phases (F_{ij}^α and F_{ij}^β , $i, j = 1, 2$) are not required to be equal and can be varied independently. For example, one of the phases can be stretched in a certain direction parallel to the incoherent interface while the other compressed in the opposite direction. This deformation produces interface sliding, which is a possible process for incoherent interfaces. Furthermore, because the lattice sites can now be created or destroyed when one phase transforms to the other, the deformation gradients \mathbf{F}^α and \mathbf{F}^β must be defined relative to *different* reference states. The incoherent phase coexistence equation would have to be re-derived from the start, which is beyond the scope of this paper.

IV. INTERFACE THERMODYNAMICS

A. The interface free energy γ

We are now ready to analyze thermodynamics of coherent interfaces. In this section we derive expressions for the interface free energy γ defined as the reversible work expended for creation of a unit interface area. As above, we imagine two coexisting phases α and β separated by a coherent plane interface (Fig. 2), but we now include the interface region as part of the system. Recall that the deformation gradients \mathbf{F}^α and \mathbf{F}^β were previously introduced for homogeneous phases and remain undefined within the highly inhomogeneous interface region. We therefore need to devise a method for introducing γ and other interface excess quantities without defining a deformation gradient inside the interface region.

As discussed earlier, the coherent two-phase equilibrium is neutral when the intensive parameters $T, M_{21}, \dots, M_{K1}, \mu_1, \dots, \mu_L, \sigma_{31}, \sigma_{32}, \sigma_{33}, F_{11}, F_{12}, F_{22}$ are fixed.⁴⁰ Consider a homogeneous region of phase α in the shape of a parallelepiped with a reference volume V' . Two faces of the parallelepiped are parallel to the interface and one edge is parallel to the x_1 axis. This is illustrated by a two-dimensional schematic in Fig. 3(b), where the parallelepiped is represented by a parallelogram. Suppose the interface spontaneously migrates and enters this region, turning it into an equilibrium two-phase system [Fig. 3(c)]. Due to the coherency condition, the cross-section of the region parallel to the interface remains the same at every height. However, the shape of the region changes due to the phase transformation strain. Consider a particular position of the interface inside the two-phase region such that the upper and lower boundaries of the region are deep inside the homogeneous phases not perturbed by the presence of the interface. Suppose the lower boundary of the region is fixed. Then the position of the upper boundary generally changes as a result of the phase transformation. Denote the displacement vector of the upper boundary \mathbf{B} .

The geometric meaning of vector \mathbf{B} is illustrated by the two-dimensional schematic in Fig. 3. The initial region $abcd$ is a deformation map of a reference region $a'b'c'd'$ with the deformation gradient \mathbf{F}^α [Fig. 3(a,b)]. After the upper part of the region transforms to phase β , it becomes a map of the corresponding upper part of the reference region with the deformation gradient \mathbf{F}^β . The reference corners c' and d' are thus mapped to some physical points c^* and d^* within the β phase [Fig. 3(c)]. Vector \mathbf{B} is defined as cc^* , or equivalently, dd^* [Fig. 3(d)]. Note that due to the conservation of sites by coherent interfaces, the two-phase region contains the same number N of substitutional sites as the initial region of phase α .

Vector \mathbf{B} is used for calculation of the mechanical work W_m performed by stresses when the discussed region transforms to the two-phase state. Since the cross-section of the region remains fixed, the mechanical work is done only by the stress components σ_{3i} when the upper boundary is displaced by vector \mathbf{B} . Thus, $W_m = A \mathbf{n}^\alpha \cdot \boldsymbol{\sigma} \cdot \mathbf{B}$, where \mathbf{n}^α is the unit normal to the interface pointing into phase β , $\mathbf{n}^\alpha \cdot \boldsymbol{\sigma}$ is the traction vector, and A is the cross-sectional area.

To keep similarity with the mechanical work terms derived previously for homogeneous phases (e.g., Eq. (30)), we want to express W_m through some deformation gradient. To this end, we *formally* define a *homogeneous* deformation gradient $\bar{\mathbf{F}}$ relative to the same reference state as used

for the homogeneous phases:

$$\bar{\mathbf{F}} := \begin{pmatrix} F_{11} & F_{12} & (F_{13}^\alpha + B_1 A'/V') \\ 0 & F_{22} & (F_{23}^\alpha + B_2 A'/V') \\ 0 & 0 & (F_{33}^\alpha + B_3 A'/V') \end{pmatrix}, \quad (38)$$

where A' is the cross-sectional area of the interface in the reference state. We will refer to $\bar{\mathbf{F}}$ as the “average” deformation gradient of the region. The geometric meaning of $\bar{\mathbf{F}}$ is the affine transformation that carries the parallelepiped representing the reference region of phase α to the parallelepiped formed by the corners of the two-phase region after the phase transformation. In the two-dimensional schematic shown in Fig. 3, $\bar{\mathbf{F}}$ transforms the reference region $a'b'c'd'$ to the parallelogram abc^*d^* . The latter is shown separately in Fig. 3(e). It should be noted that both \mathbf{B} and $\bar{\mathbf{F}}$ generally depend on the choice of the reference thickness V'/A' of the α phase region and on the position of the interface within the two-phase region. In terms of $\bar{\mathbf{F}}$, the mechanical work term can now be rewritten as

$$W_m = A \sum_{i=1,2,3} \sigma_{3i} B_i = \sum_{i=1,2,3} (V \bar{F}_{i3} / \bar{F}_{33} - V^\alpha F_{i3}^\alpha / F_{33}^\alpha) \sigma_{3i}, \quad (39)$$

where $V^\alpha = F_{11} F_{22} F_{33}^\alpha V'$ and $V = F_{11} F_{22} \bar{F}_{33} V'$ are physical volumes of the α phase region and the two-phase region, respectively.⁴¹

We next calculate the change in internal energy of the region when it reversibly transforms from phase α to the two-phase state [Fig. 3(b,c)]. Instead of tracking the actual motion of the interface into the region, we will consider only the initial and final states and imagine a different reversible process between them. Specifically, consider a process of homogeneous phase transformation $\alpha \rightarrow \beta$ in the upper part of the region at fixed N and fixed intensive parameters $T, M_{21}, \dots, M_{K1}, \mu_1, \dots, \mu_L, \sigma_{31}, \sigma_{32}, \sigma_{33}, F_{11}, F_{12}, F_{22}$. Since the transformation occurs in an open system, its energy changes due to the following processes: (i) heat exchange with the environment, (ii) diffusion of atoms in and out of the system (at constant N), (iii) mechanical work W_m performed by stresses applied to the boundaries of the region, and (iv) non-mechanical work W_{nm} associated with local atomic rearrangements leading to the formation of the interface. Using Eq. (39) for W_m , we have

$$\begin{aligned}
U - U^\alpha = & T(S - S^\alpha) + \sum_{k=2}^K M_{k1} (N_k - N_k^\alpha) + \sum_{l=1}^L \mu_l (n_l - n_l^\alpha) \\
& + \sum_{i=1,2,3} (V\bar{F}_{i3}/\bar{F}_{33} - V^\alpha F_{i3}^\alpha/F_{33}^\alpha) \sigma_{3i} + W_{nm},
\end{aligned} \tag{40}$$

where the extensive quantities with and without superscript α refer to the initial and final states, respectively.

We define the interface free energy γ as the non-mechanical work done per unit interface area, i.e., $\gamma A := W_{nm}$. Using Eq. (17) for the α phase, Eq. (40) can be simplified to

$$\gamma A = U - TS - \sum_{k=2}^K M_{k1} N_k - \phi_1 N - \sum_{l=1}^L \mu_l n_l - \sum_{i=1,2,3} (V\bar{F}_{i3}/\bar{F}_{33}) \sigma_{3i}, \tag{41}$$

or expressing the diffusion potentials through the ϕ -potentials using Eq. (19),

$$\gamma A = U - TS - \sum_{k=1}^K \phi_k N_k - \sum_{l=1}^L \mu_l n_l - \sum_{i=1,2,3} (V\bar{F}_{i3}/\bar{F}_{33}) \sigma_{3i}. \tag{42}$$

These equations can be rewritten in a shorter form by introducing the Φ_1 potential of a two-phase region by analogy with Eq. (13):

$$\Phi_1 := U - TS - \sum_{k=2}^K M_{k1} N_k - \sum_{l=1}^L \mu_l n_l - \sum_{i=1,2,3} (V\bar{F}_{i3}/\bar{F}_{33}) \sigma_{3i}. \tag{43}$$

Then

$$\gamma A = \Phi_1 - N\phi_1, \tag{44}$$

so that γ is an excess of the Φ_1 potential per unit interface area. Of course, instead of component 1 we could have chosen any other substitutional component as a reference.

Eqs. (41) and (42) express the total interface free energy γA through properties of an arbitrary region containing the interface. While γA is uniquely defined by these equations, the individual terms appearing in the right-hand side depend on the location of the boundaries of the region. To express these terms through interface excesses that are independent of the boundaries, we need to subtract the contributions of the homogeneous phases. To this end, we select two arbitrary regions inside the homogeneous phases. Such single-phase regions can be chosen either inside or outside the two-phase region. The latter case is illustrated in Fig. 4. Let the total numbers of substitutional

atoms in the single-phase regions be N^α and N^β , respectively (generally, $N^\alpha \neq N^\beta$). Eq. (17) applied to these regions gives

$$0 = U^\alpha - TS^\alpha - \sum_{k=2}^K M_{k1} N_k^\alpha - \phi_1 N^\alpha - \sum_{l=1}^L \mu_l n_l^\alpha - \sum_{i=1,2,3} (VF_{i3}/F_{33})^\alpha \sigma_{3i} \quad (45)$$

and

$$0 = U^\beta - TS^\beta - \sum_{k=2}^K M_{k1} N_k^\beta - \phi_1 N^\beta - \sum_{l=1}^L \mu_l n_l^\beta - \sum_{i=1,2,3} (VF_{i3}/F_{33})^\beta \sigma_{3i}. \quad (46)$$

Eqs. (41), (45) and (46) form a system of three linear equations with respect to the same intensive variables. We solve this system of equations for γA using Cramer's rule of linear algebra.⁸ The solution has the form

$$\gamma A = [U]_{XY} - T[S]_{XY} - \sum_{k=2}^K M_{k1} [N_k]_{XY} - \phi_1 [N]_{XY} - \sum_{l=1}^L \mu_l [n_l]_{XY} - \sum_{i=1,2,3} [V\bar{F}_{i3}/\bar{F}_{33}]_{XY} \sigma_{3i}, \quad (47)$$

where X and $Y \neq X$ are any two of the extensive quantities U , S , N_k ($k = 2, \dots, K$), N , n_l ($l = 1, \dots, L$) or $V\bar{F}_{i3}/\bar{F}_{33}$ ($i = 1, 2, 3$). Note that the last member of this list, corresponding to $i = 3$, is simply volume V . Using Eq. (19) we obtain the equivalent form of γA :

$$\gamma A = [U]_{XY} - T[S]_{XY} - \sum_{k=1}^K \phi_k [N_k]_{XY} - \sum_{l=1}^L \mu_l [n_l]_{XY} - \sum_{i=1,2,3} [V\bar{F}_{i3}/\bar{F}_{33}]_{XY} \sigma_{3i}. \quad (48)$$

The coefficients $[Z]_{XY}$ are computed as ratios of two determinants:⁶

$$[Z]_{XY} := \frac{\begin{vmatrix} Z & X & Y \\ Z^\alpha & X^\alpha & Y^\alpha \\ Z^\beta & X^\beta & Y^\beta \end{vmatrix}}{\begin{vmatrix} X^\alpha & Y^\alpha \\ X^\beta & Y^\beta \end{vmatrix}}. \quad (49)$$

The quantities in the first row of the numerator are computed for the region containing the interface, whereas all other quantities are computed for arbitrary homogeneous regions of phases α and β . By properties of determinants,

$$[X]_{XY} = [Y]_{XY} = 0, \quad (50)$$

so that two terms in each of the Eqs. (47) and (48) automatically vanish.

The coefficient $[Z]_{XY}$ has the meaning of the interface excess of extensive property Z when the region containing the interface contains the same amounts of X and Y as the two single-phase regions combined; in other words, when the excesses of X and Y are zero. Thus, the excess of any property Z is not unique; it generally depends on the choice of the reference properties X and Y . If either X or Y is volume, then $[Z]_{XY}$ has the meaning of the excess of Z relative to a dividing surface similar to Gibbs' formulation of interface thermodynamics.³

The excesses $[N_k]_{XY}$ and $[n_l]_{XY}$ characterize the segregated amounts of substitutional and interstitial components, respectively. The terms $[V]_{XY}$, $[V\bar{F}_{13}/\bar{F}_{33}]_{XY}$ and $[V\bar{F}_{23}/\bar{F}_{33}]_{XY}$ define the excess volume and two excess shears, respectively. For example,

$$[V\bar{F}_{i3}/\bar{F}_{33}]_{SV} = \frac{\begin{vmatrix} V\bar{F}_{i3}/\bar{F}_{33} & S & V \\ (VF_{i3}/F_{33})^\alpha & S^\alpha & V^\alpha \\ (VF_{i3}/F_{33})^\beta & S^\beta & V^\beta \end{vmatrix}}{\begin{vmatrix} S^\alpha & V^\alpha \\ S^\beta & V^\beta \end{vmatrix}}, \quad i = 1, 2. \quad (51)$$

In this case, the excess shears are taken with respect to a dividing surface for which the excess of entropy is zero. The excess shears are properties specific to coherent interfaces. They have no significance for incoherent solid-solid interfaces, solid-fluid interfaces or any other interfaces that cannot be equilibrated under applied shear stresses. By contrast, the excess volume $[V]_{XY}$ is common to all types of interfaces.⁶ The numerical values of the excess volume and excess shears depend on the choice of the reference properties X and Y . In the Gibbian formalism of dividing surface the excess volume is zero by definition.

The total interface free energy γA can be expressed through excesses of different thermodynamic potentials corresponding to possible choices of X and Y . As already noted, γA can be expressed as an excess of potential Φ_1 . Using our square bracket notation,

$$\gamma A = [U - TS - \sum_{k=2}^K M_{k1} N_k - \sum_{l=1}^L \mu_l n_l - \sum_{i=1,2} (V\bar{F}_{i3}/\bar{F}_{33}) \sigma_{3i}]_{NV} \equiv [\Phi_1]_{NV}, \quad (52)$$

i.e., the excess of Φ_1 must be taken relative to the dividing surface for which the excess of the total number of substitutional atoms is zero. As another example,

$$\gamma A = [U - \sum_{k=2}^K M_{k1} N_k - \sum_{l=1}^L \mu_l n_l - \sum_{i=1,2,3} (V \bar{F}_{i3} / \bar{F}_{33}) \sigma_{3i}]_{NS}, \quad (53)$$

i.e., γA is an excesses of the potential appearing in the square brackets when the excesses of the total number of substitutional atoms and entropy are zero. The flexibility in expressing the same quantity γA through excesses of different thermodynamic potentials can be useful in applications of this formalism to experimental measurements and simulations.

B. The adsorption equation

Having introduced the interface free energy, we are now in a position to derive the generalized adsorption equation for coherent interfaces. As the first step, we will compute the energy differential dU for a two-phase region containing the interface. We will take a region in the shape of a parallelepiped as shown schematically in Fig. 3(e). Recall that this shape is a map of the reference region of phase α containing the same number of substitutional atoms as in the parallelepiped. This deformation map is formally defined by the deformation gradient $\bar{\mathbf{F}}$ given by Eq. (38). Consider a reversible variation in which this region exchanges heat and atoms with its environment (at fixed N) and performs mechanical work by elastically changing its shape and dimensions. The mechanical work, dW_m , is done by the stresses applied to all faces of the parallelepiped and equals the sum of the total forces exerted on the faces times their displacements. The calculations give

$$dW_m = \sum_{i=1,2,3} V' F_{11} F_{22} \sigma_{3i} d\bar{F}_{i3} + \sum_{i,j=1,2} V' \bar{P}_{ij} dF_{ji}, \quad (54)$$

where $\bar{\mathbf{P}} := \bar{J} \bar{\mathbf{F}}^{-1} \cdot \bar{\boldsymbol{\sigma}}$ is a formal analog of the first Piola-Kirchhoff stress tensor, $\bar{\boldsymbol{\sigma}}$ is the true stress tensor averaged over the volume of the parallelepiped, $\bar{J} := \det \bar{\mathbf{F}}$, and V' is the reference volume of the phase α region. Because the stress components σ_{3i} are coordinate-independent and the lateral stress components σ_{ij} ($i, j = 1, 2$) depend only on the coordinate x_3 , it is only the lateral stress components that must be averaged over x_3 in order to obtain $\bar{\boldsymbol{\sigma}}$. Using the above expression for dW_m , the energy differential equals

$$\begin{aligned} dU = & TdS + \sum_{k=2}^K M_{k1} dN_k + \sum_{l=1}^L \mu_l dn_l \\ & + \sum_{i=1,2,3} V' F_{11} F_{22} \sigma_{3i} d\bar{F}_{i3} + \sum_{i,j=1,2} V' \bar{P}_{ij} dF_{ji}. \end{aligned} \quad (55)$$

This equation looks similar to the previously derived Eq. (12) and constitutes its generalization to inhomogeneous systems containing a coherent interface.

At the next step, we take the differential of Eq. (41) and insert dU from Eq. (55). After some rearrangement we obtain

$$\begin{aligned} d(\gamma A) = & -SdT - \sum_{k=2}^K N_k dM_{k1} - Nd\phi_1 - \sum_{l=1}^L n_l d\mu_l \\ & - \sum_{i=1,2,3} (V\bar{F}_{i3}/\bar{F}_{33}) d\sigma_{3i} + \sum_{i,j=1,2} V'\bar{Q}_{ij} dF_{ji} = d\Phi_1 - Nd\phi_1, \end{aligned} \quad (56)$$

where we introduced the tensor

$$\bar{\mathbf{Q}} := \bar{J}\bar{\mathbf{F}}^{-1} \cdot \left(\bar{\boldsymbol{\sigma}} - \sum_{m=1,2,3} \frac{\bar{F}_{m3}}{\bar{F}_{33}} \sigma_{3m} \mathbf{I} \right). \quad (57)$$

For a homogeneous phase, $\bar{\mathbf{Q}}$ reduces to the earlier introduced tensor \mathbf{Q} , see Eq. (16).

The differentials in the right-hand side of Eq. (56) are not independent. There are two constraints imposed by the Gibbs-Duhem equations (33) and (34) containing the same differentials. Solving the system of equations (56), (33) and (34) by Cramer's rule, we finally obtain the generalized adsorption equation

$$\begin{aligned} d(\gamma A) = & -[S]_{XY} dT - \sum_{k=2}^K [N_k]_{XY} dM_{k1} - [N]_{XY} d\phi_1 - \sum_{l=1}^L [n_l]_{XY} d\mu_l \\ & - \sum_{i=1,2,3} [V\bar{F}_{i3}/\bar{F}_{33}]_{XY} d\sigma_{3i} + \sum_{i,j=1,2} [V'\bar{Q}_{ij}]_{XY} dF_{ji}, \end{aligned} \quad (58)$$

where X and Y are two of the extensive properties S , N_k ($k = 2, \dots, K$), N , n_l ($l = 1, \dots, L$), $V\bar{F}_{i3}/\bar{F}_{33}$ ($i = 1, 2, 3$) or $V'\bar{Q}_{ij}$ ($i, j = 1, 2$).

Note the significant difference between Eqs. (56) and (58) written for the same differential $d(\gamma A)$. In Eq. (56), the differential coefficients are properties of the entire region containing the interface. These properties depend on the choice of the boundaries of the region and thus have no physical significance. In the adsorption equation (58), on the other hand, the differential coefficients are interface excesses $[Z]_{XY}$ defined by Eq. (49). For a given choice of the reference properties X and Y , such excesses are independent of the boundaries of the region. Furthermore, the number of differentials in the right-hand side of Eq. (56) exceeds the number $(K + L + 5)$ of degrees of freedom of a coherent two-phase system predicted by Eq. (35). By contrast, due to the property (50) of determinants, two terms in Eq. (58) automatically vanish, leaving exactly

$(K + L + 5)$ independent differentials. Each of the remaining excesses $[Z]_{XY}$ can be expressed as a partial derivative of γA with respect to the corresponding intensive variable and is therefore a measurable physical quantity. In terms of the ϕ -potentials, the adsorption equation takes the form

$$\begin{aligned} d(\gamma A) = & -[S]_{XY}dT - \sum_{k=1}^K [N_k]_{XY}d\phi_k - \sum_{l=1}^L [n_l]_{XY}d\mu_l \\ & - \sum_{i=1,2,3} [V\bar{F}_{i3}/\bar{F}_{33}]_{XY}d\sigma_{3i} + \sum_{i,j=1,2} [V'\bar{Q}_{ij}]_{XY}dF_{ji}. \end{aligned} \quad (59)$$

The adsorption equation corresponding to Gibbs' formalism of the dividing surface is obtained as a particular case of our adsorption equation when either $X = V$ or $Y = V$. Although the excess volume $[V]_{XY}$ disappears, the excess shears $[V\bar{F}_{i3}/\bar{F}_{33}]_{XY}$ and $[V'\bar{Q}_{ij}]_{XY}$ still remain. These additional terms are not present in Gibbs' interface thermodynamics³ or in Cahn's work.⁶

C. The interface stress

The terms in the adsorption equation that contain differentials of the lateral deformation components F_{11} , F_{12} and F_{22} represent contributions to γA coming from elastic deformations of the interface. These terms define the interface stress, the quantity which was first discussed by Gibbs in the context of solid-fluid interfaces.³

To formally define the interface stress tensor, choose the current state of one of the phases as the reference state of strain. Then $F_{11} = F_{22} = 1$, $F_{12} = 0$, and Eq. (58) becomes

$$\begin{aligned} d(\gamma A) = & -[S]_{XY}dT - \sum_{k=2}^K [N_k]_{XY}dM_{k1} - [N]_{XY}d\phi_1 - \sum_{l=1}^L [n_l]_{XY}d\mu_l \\ & - \sum_{i=1,2,3} [V\bar{F}_{i3}/\bar{F}_{33}]_{XY}d\sigma_{3i} + \sum_{i,j=1,2} \tau_{ij}^{XY} Ade_{ji}, \end{aligned} \quad (60)$$

where

$$\tau_{11}^{XY} := \frac{1}{A}[V'\bar{Q}_{11}]_{XY}, \quad \tau_{22}^{XY} := \frac{1}{A}[V'\bar{Q}_{22}]_{XY}, \quad \tau_{12}^{XY} = \tau_{21}^{XY} := \frac{1}{A}[V'\bar{Q}_{12}]_{XY}. \quad (61)$$

In Eq. (60), de is a (2×2) small-strain tensor with components $de_{11} = dF_{11}$, $de_{22} = dF_{22}$ and $de_{12} = de_{21} = \frac{1}{2}dF_{12}$. The (2×2) symmetrical tensor τ defined by Eqs. (61) is the interface stress tensor describing changes in the interface free energy due to its elastic deformations.

As other interface excess quantities, τ generally depends on the choice of the reference properties X and Y and is therefore not unique. However, in the particular case when both phases are

in a hydrostatic state of stress under a pressure p , τ becomes independent of X and Y and is given by

$$\tau_{ij} = \frac{V}{A} (\bar{\sigma}_{ij} + p\delta_{ij}). \quad i, j = 1, 2. \quad (62)$$

This equation immediately follows from the definition of the square bracket $[V'\bar{Q}_{ij}]_{XY}$ and the fact that for hydrostatic phases $\bar{Q}_{ij}^\alpha = \bar{Q}_{ij}^\beta = 0$.

Eqs. (61) provide a recipe for interface stress calculation when the phases are subject to non-hydrostatic stresses, particularly when such stresses are different in the two phases (e.g., when one phase is under lateral tension while the other under lateral compression). Previous calculations of interface stresses were focused on unstressed or hydrostatically stressed phases. For solid-fluid interfaces, the calculations for hydrostatic phases employed equations similar to (62). Non-hydrostatic stresses were included only in surface stress calculations in single-phase systems.⁷ Calculations of τ between non-hydrostatic solid phases using Eqs. (61) is an uncharted territory and could be addressed in future work.

In the remainder of this paper, the lateral deformations of a two-phase system will be described by the small-strain tensor de instead of the lateral components of the deformation gradient. As mentioned above, this implies that the current state of one of the phases is chosen as the reference state of strain. It should be emphasized that (i) this assumption only reflects a particular choice of the kinematic description of deformations, not a physical approximation, and (ii) the normal and shear components F_{i3} describing the transformation strain between the two phases can still be finite.

D. Lagrangian and physical forms of the adsorption equation

Until this point we dealt with total excess quantities related to the entire interface with an area A . It is often useful to define *specific* excesses, i.e. excesses per unit interface area in either the current state or the reference state of strain. In the former case, the excess quantity is referred to as physical while in the latter case as Lagrangian. For example, γ is the physical specific excess of the interface free energy. The interface stress defined by Eq. (61) is the physical specific excess of the tensor quantity $V'\bar{Q}_{ij}$. One can also define the Lagrangian interface free energy, $\gamma_L := (\gamma A)/A'$, and the Lagrangian interface stress,

$$\tau_{L11}^{XY} := \frac{1}{A'} [V'\bar{Q}_{11}]_{XY}, \quad \tau_{L22}^{XY} := \frac{1}{A'} [V'\bar{Q}_{22}]_{XY}, \quad \tau_{L12}^{XY} = \tau_{L21}^{XY} := \frac{1}{A'} [V'\bar{Q}_{12}]_{XY}. \quad (63)$$

Using Eq. (63) and the adsorption equation (58), we obtain the relation

$$\tau_{Lij}^{XY} = \left(\frac{\partial \gamma_L}{\partial e_{ij}} \right)^{XY}. \quad (64)$$

A similar relation involving the Lagrangian γ was proposed by Cahn.⁶ Here, the superscript XY in the right-hand side indicates that the partial derivative is taken at fixed intensive parameters, other than e_{ij} , that appear in the adsorption equation when X and Y are chosen as the reference properties.

The Lagrangian form of the adsorption equation is obtained by dividing Eq. (60) by A' :

$$\begin{aligned} d\gamma_L = & -\frac{[S]_{XY}}{A'}dT - \sum_{k=2}^K \frac{[N_k]_{XY}}{A'}dM_{k1} - \frac{[N]_{XY}}{A'}d\phi_1 - \sum_{l=1}^L \frac{[n_l]_{XY}}{A'}d\mu_l \\ & - \sum_{i=1,2,3} \frac{[V\bar{F}_{i3}/\bar{F}_{33}]_{XY}}{A'}d\sigma_{3i} + \sum_{i,j=1,2} \tau_{Lij}^{XY} de_{ji}, \end{aligned} \quad (65)$$

where the differential coefficients are Lagrangian specific excesses. The physical form of the adsorption equation is obtained by differentiating γA in Eq. (60) and using the relation $dA = A \sum_{i,j=1,2} \delta_{ij} de_{ij}$:

$$\begin{aligned} d\gamma = & -\frac{[S]_{XY}}{A}dT - \sum_{k=2}^K \frac{[N_k]_{XY}}{A}dM_{k1} - \frac{[N]_{XY}}{A}d\phi_1 - \sum_{l=1}^L \frac{[n_l]_{XY}}{A}d\mu_l \\ & - \sum_{i=1,2,3} \frac{[V\bar{F}_{i3}/\bar{F}_{33}]_{XY}}{A}d\sigma_{3i} + \sum_{i,j=1,2} (\tau_{ij}^{XY} - \delta_{ij}\gamma) de_{ji}. \end{aligned} \quad (66)$$

Now the differential coefficients give physical specific excesses. From this equation, we immediately obtain the generalized form of the Shuttleworth equation:⁴

$$\left(\frac{\partial \gamma}{\partial e_{ij}} \right)^{XY} = \tau_{ij}^{XY} - \delta_{ij}\gamma. \quad (67)$$

The original Shuttleworth equation⁴ was derived for an open surface of a stress-free single-component solid deformed isothermally. Eq. (67) has been derived for coherent interfaces in multicomponent systems in an arbitrary state of stress. It actually represents a set of equations corresponding to different choices of X and Y and thus different deformation paths.

Just as the Shuttleworth equation describes the effect of lateral strains on the interface free energy, the following equations describe the effect of the shear and normal stresses of γ and γ_L in the physical and Lagrangian forms, respectively:

$$\left(\frac{\partial \gamma}{\partial \sigma_{3i}} \right)^{XY} = \frac{[V\bar{F}_{i3}/\bar{F}_{33}]_{XY}}{A}, \quad i = 1, 2, 3, \quad (68)$$

$$\left(\frac{\partial \gamma_L}{\partial \sigma_{3i}}\right)^{XY} = \frac{[V\bar{F}_{i3}/\bar{F}_{33}]_{XY}}{A'}, \quad i = 1, 2, 3. \quad (69)$$

E. Thermodynamic integration

We will now derive another version of the adsorption equation that can be useful in applications. In principle, the interface free energy γ can be computed by integration of the adsorption equation along a phase coexistence path knowing an initial value. However, the excess entropy $[S]_{XY}$ appearing in this equation is rarely accessible by experiments or simulations. To avoid calculation of $[S]_{XY}$, we can eliminate it by combining Eqs. (47) and (60) to obtain

$$\begin{aligned} d\left(\frac{\gamma A}{T}\right) = & -\frac{[\Psi]_{XY}}{T^2}dT - \sum_{k=2}^K \frac{[N_k]_{XY}}{T}dM_{k1} - \frac{[N]_{XY}}{T}d\phi_1 - \sum_{l=1}^L \frac{[n_l]_{XY}}{T}d\mu_l \\ & - \sum_{i=1,2,3} \frac{[V\bar{F}_{i3}/\bar{F}_{33}]_{XY}}{T}d\sigma_{3i} + \frac{1}{T} \sum_{i,j=1,2} \tau_{ij}^{XY} Ade_{ji}, \end{aligned} \quad (70)$$

where the thermodynamic potential Ψ is defined by

$$\Psi := U - \sum_{k=2}^K N_k M_{k1} - N\phi_1 - \sum_{l=1}^L n_l d\mu_l - \sum_{i=1,2,3} \sigma_{3i} V\bar{F}_{i3}/\bar{F}_{33}. \quad (71)$$

It is straightforward to derive physical and Lagrangian forms of this equation, whose left-hand sides will contain $d(\gamma/T)$ and $d(\gamma_L/T)$, respectively.

In the particular case when only temperature is varied, Eq. (70) gives

$$\left(\frac{\partial(\gamma A/T)}{\partial T}\right)^{XY} = -\frac{[\Psi]_{XY}}{T^2}. \quad (72)$$

This equation is similar to the classical Gibbs-Helmholtz equation²¹

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{U + pV}{T^2} \quad (73)$$

for single-component fluid systems. Eq. (70) can be viewed as a generalization of the Gibbs-Helmholtz equation to interfaces in multicomponent systems.

Eq. (70) can be used to compute γ by integration of $\gamma A/T$ along a trajectory on the phase coexistence hypersurface in the configuration space of variables. The advantage of this integration is that it does not require knowledge of $[S]_{XY}$. Free energy calculations for solid-solid interfaces in multi-component elastically stressed systems are presently non-existent and could be initiated by applying the proposed thermodynamic integration approach.

F. Maxwell relations

Because the adsorption equation contains the perfect differential of γA , it generates a number of Maxwell relations between partial derivatives of the excess quantities. Similarly, the Gibbs-Helmholtz equation (70) is the perfect differential of $\gamma A/T$ and also generates Maxwell relations. We will focus on Maxwell relations that involve the effects of mechanical stresses and strains on interface properties. For hydrostatic precesses, such relations were discussed by Cahn.⁶ The additional terms in the adsorption equation introduced in this work, such as the variations in the shear stresses σ_{31} and σ_{32} , lead to a number of additional Maxwell relations. The Lagrangian and physical forms of the adsorption equation produce different Maxwell relations, which will be presented below side by side. In the partial derivatives appearing in these relations, the variables which are held constant are dictated by the particular choice of the extensive variables X and Y . Thus, each Maxwell relation actually represents a set of relations corresponding to different choices of X and Y .

1. Mechanical relations

The first set of Maxwell relations examines how the lateral deformations de_{ij} and the stresses σ_{3k} affect the interface excess volume, excess shears and interface stress. Using the Lagrangian and physical forms of the adsorption equation, we obtain

$$\frac{\partial \tau_{Lij}^{XY}}{\partial e_{kl}} = \frac{\partial \tau_{Lkl}^{XY}}{\partial e_{ij}}, \quad \frac{\partial (\tau_{ij}^{XY} - \delta_{ij}\gamma)}{\partial e_{kl}} = \frac{\partial (\tau_{kl}^{XY} - \delta_{kl}\gamma)}{\partial e_{ij}}, \quad (74)$$

$$i, j, k, l = 1, 2,$$

$$\frac{\partial \tau_{Lij}^{XY}}{\partial \sigma_{33}} = -\frac{\partial ([V]_{XY}/A')}{\partial e_{ij}}, \quad \frac{\partial (\tau_{ij}^{XY} - \delta_{ij}\gamma)}{\partial \sigma_{33}} = -\frac{\partial ([V]_{XY}/A)}{\partial e_{ij}}, \quad (75)$$

$$i, j = 1, 2,$$

$$\frac{\partial \tau_{Lij}^{XY}}{\partial \sigma_{3k}} = -\frac{\partial ([VF_{k3}/F_{33}]_{XY}/A')}{\partial e_{ij}}, \quad \frac{\partial (\tau_{ij}^{XY} - \delta_{ij}\gamma)}{\partial \sigma_{3k}} = -\frac{\partial ([VF_{k3}/F_{33}]_{XY}/A)}{\partial e_{ij}}, \quad (76)$$

$$i, j, k = 1, 2,$$

$$\frac{\partial ([VF_{k3}/F_{33}]_{XY}/A')}{\partial \sigma_{33}} = \frac{\partial ([V]_{XY}/A')}{\partial \sigma_{3k}}, \quad k = 1, 2. \quad (77)$$

Eq. (74) represents the effect of lateral deformations on the interface stress. Eq. (75) describes the interfacial Poisson effect, in which lateral deformations of the interface produce changes in the “interface thickness” (excess volume per unit area). Because Eqs. (74)-(76) involve changes in interface area, their Lagrangian and physical forms are different. By contrast, in Eq. (77) the derivatives are taken at a constant area and thus the Lagrangian and physical forms are identical. In such cases we present only the Lagrangian form of the relation.

2. Mechanochemical relations

Elastic deformations parallel or normal to the interface affect interface segregation. In turn, changes in segregation can produce changes in interface stress, interface excess volume and interface excess shears. We will present only Maxwell relations for substitutional components when the diffusion potentials M_{k1} are varied. For interstitial components, the relations have a similar form but with the diffusion potentials replaced by the chemical potentials μ_l . The effect of deformations parallel to the interface on the interface segregation is described by the relations

$$\frac{\partial \tau_{Lij}^{XY}}{\partial M_{k1}} = -\frac{\partial ([N_k]_{XY}/A')}{\partial e_{ij}}, \quad \frac{\partial (\tau_{ij}^{XY} - \delta_{ij}\gamma)}{\partial M_{k1}} = -\frac{\partial ([N_k]_{XY}/A)}{\partial e_{ij}}, \quad (78)$$

$i, j = 1, 2; \quad k = 2, \dots, K.$

Because the interface area changes, the Lagrangian and physical forms of this relation are different. The effect of the stress components σ_{31} , σ_{32} and σ_{33} on segregation is described by the relations

$$\frac{\partial ([V]_{XY}/A')}{\partial M_{k1}} = \frac{\partial ([N_k]_{XY}/A')}{\partial \sigma_{33}}, \quad k = 2, \dots, K, \quad (79)$$

$$\frac{\partial ([VF_{i3}/F_{33}]_{XY}/A')}{\partial M_{k1}} = \frac{\partial ([N_k]_{XY}/A')}{\partial \sigma_{3i}}, \quad i = 1, 2; \quad k = 2, \dots, K. \quad (80)$$

Since the derivatives are taken at a constant area, the Lagrangian and physical forms are identical.

3. Thermomechanical relations

Such relations describe the effects of temperature on interface stress, excess volume and excess shears. The relations generated by the adsorption equation would contain the excess entropy $[S]_{XY}$ which is not easily accessible. Instead, we will use the Gibbs-Helmholtz equation (70) which does not contain $[S]_{XY}$. The following Maxwell relations are obtained:

$$\frac{\partial (\tau_{Lij}^{XY}/T)}{\partial T} = -\frac{\partial ([\Psi]_{XY}/A'T^2)}{\partial e_{ij}}, \quad \frac{\partial \{(\tau_{ij}^{XY} - \delta_{ij}\gamma)/T\}}{\partial T} = -\frac{\partial ([\Psi]_{XY}/AT^2)}{\partial e_{ij}}, \quad (81)$$

$i, j = 1, 2,$

$$\frac{\partial ([V]_{XY}/A'T)}{\partial T} = \frac{\partial ([\Psi]_{XY}/A'T^2)}{\partial \sigma_{33}}, \quad (82)$$

$$\frac{\partial ([VF_{k3}/F_{33}]_{XY}/A'T)}{\partial T} = \frac{\partial ([\Psi]_{XY}/A'T^2)}{\partial \sigma_{3k}}, \quad k = 1, 2. \quad (83)$$

where the potential Ψ is given by Eq. (71). In Eq. (81), the Lagrangian and physical forms of the same relation are different.

4. Thermochemical relations

Using the Gibbs-Helmholtz equation (70), we can evaluate the effect of temperature on interface segregation of substitutional and interstitial components. The corresponding derivatives involve the excess $[\Psi]_{XY}$ instead of $[S]_{XY}$ and read

$$\frac{\partial ([N_k]_{XY}/A'T)}{\partial T} = \frac{\partial ([\Psi]_{XY}/A'T^2)}{\partial M_{k1}}, \quad k = 2, \dots, K, \quad (84)$$

$$\frac{\partial ([n_l]_{XY}/A'T)}{\partial T} = \frac{\partial ([\Psi]_{XY}/A'T^2)}{\partial \mu_l}. \quad l = 1, \dots, L. \quad (85)$$

For substitutional components, the derivatives are taken with respect to diffusion potentials, whereas for interstitial components with respect to chemical potentials. The Lagrangian and physical forms of these relations are identical.

V. RELATION TO OTHER TYPES OF INTERFACES

A. Incoherent solid-solid interfaces

Incoherent solid-solid interfaces differ from coherent in two ways:

1. Lateral deformations of the two phases are allowed to be different and independent of each other, as long as they preserve the orientation of the interface plane. Accordingly, the deformation gradients of the phases must still have the upper-triangular form but need not satisfy Eqs. (25) and (26) with equal lateral components.

2. Incoherent interfaces do not support static shear stresses applied parallel to the interface plane, responding to such stresses by sliding.

These conditions can be reconciled with the coherent interface theory by considering only processes in which the shear stresses σ_{31} and σ_{32} are identically zero and the lateral deformations of the phases remain equal. Under these constraints, the incoherency of the interface does not manifest itself and all equations derived for coherent interfaces are valid for incoherent ones. The number of independent variables reduces to $(K + L + 3)$ and all equations are significantly simplified. In particular, the equations no longer contain the components \bar{F}_{i3} of the deformation gradient $\bar{\mathbf{F}}$ [Eq. (38)] and the latter need not be introduced. The shapes of the two-phase and single-phase regions used in the thought experiments become unimportant; only their volumes appear in the final equations.

For example, the total interface free energy γA is given by the simplified form of Eq. (48),

$$\gamma A = [U]_{XY} - T[S]_{XY} - \sum_{k=1}^K \phi_k [N_k]_{XY} - \sum_{l=1}^L \mu_l [n_l]_{XY} - [V]_{XY} \sigma_{33}. \quad (86)$$

The potentials ϕ_m defined by Eq. (18) reduce to

$$\phi_m = U/N - TS/N - \sum_{k=1}^K M_{km} C_k - \sum_{l=1}^L \mu_l c_l - \sigma_{33} \Omega. \quad (87)$$

The adsorption equation becomes

$$d(\gamma A) = -[S]_{XY} dT - \sum_{k=1}^K [N_k]_{XY} d\phi_k - \sum_{l=1}^L [n_l]_{XY} d\mu_l - [V]_{XY} d\sigma_{33} + \sum_{i,j=1,2} \tau_{ij}^{XY} A de_{ji}, \quad (88)$$

where we use the current state of one of the phases as the reference state of lateral strain. The interface stress tensor simplifies to

$$\tau_{ij}^{XY} = \frac{1}{A} [V (\bar{\sigma}_{ij} - \sigma_{33} \delta_{ij})]_{XY}, \quad (89)$$

where $\bar{\sigma}_{ij}$ is the Cauchy stress tensor averaged over a region of volume V .

It should be emphasized, however, that the above equations describe only some of the possible state variations of an incoherent two-phase systems. They do not include variations in which the phases undergo different lateral deformations and thus slip against each other. Due to such variations, an incoherent two-phase system possesses more degrees of freedom than a coherent one with the same number of substitutional and interstitial components. Thus, incoherent interfaces cannot be considered a particular case of coherent interfaces. They require a separate treatment, which will be presented elsewhere.

B. Grain boundaries

Grain boundary is an interface between regions of the same crystalline phase with different lattice orientations. As other solid-solid interfaces, GBs can be coherent or incoherent. Coherent GBs can support not only stresses normal to the GB plane but also shear stresses parallel to it. When temperature²² and/or chemical composition²³ change, some coherent GBs can change their structure to one that permits GB sliding. The GB becomes incoherent.

Two different cases must be distinguished: when the grains are thermodynamically identical and when they are not. By definition, the grains are considered thermodynamically identical when the phase-change equilibrium condition (30) is satisfied as a mathematical identity once the equilibrium conditions (i)-(iv) formulated in Section III B are satisfied. In other words, the phase-change equilibrium condition need not be imposed as a separate equation of constraint. This can be the case when the grains are stress-free and uninfluenced by electric, magnetic or other fields. Thermodynamically identical grains can be treated as parts of the same single-phase system. On the other hand, in the presence of mechanical stresses or applied fields, the equilibrium thermodynamic states of the grains can be different. For example, when the solid is elastically anisotropic and the grains are subject to mechanical stresses, they either never reach equilibrium or can reach an equilibrium state in which their elastic strain energy densities and chemical compositions are different. In the latter case, the phase-change equilibrium condition (30) is not satisfied automatically and must be imposed as a separate constraint. Such cases should be formally treated as if the grains were two different phases. Accordingly, all thermodynamic equations developed in Sections III and IV for phase boundaries directly apply to this case.

There are situations when, due to crystal symmetry, the grains remain thermodynamically identical even in the presence of certain mechanical stresses. As an example, consider a coherent symmetrical tilt GB. In the unstressed state, the grains are identical and form a single-phase system. Due to the mirror symmetry across the boundary plane, the lateral deformations de_{ij} ($i, j = 1, 2$) and the normal stress σ_{33} leave the grains identical. Moreover, due to the twofold symmetry around the axis x_2 normal to the tilt axis, the shear stress σ_{31} also leaves the grains identical. Thus, when the system is subject to these deformations, it continues to be a single-phase system.⁴² That Eq. (30) is satisfied in this case as an identity can be seen from the fact that the differences $(U^\beta - U^\alpha)$, $(S^\beta - S^\alpha)$, $(N_k^\beta - N_k^\alpha)$ and $(n_l^\beta - n_l^\alpha)$ related to grain regions containing the same total numbers of substitutional atoms are zero by the symmetry. The remaining terms in Eq. (30)

represent the mechanical work W_m and are given by Eq. (31). For a symmetrical tilt boundary $F_{13}^\beta = F_{13}^\alpha$ and $F_{33}^\beta = F_{33}^\alpha$; only the shear components F_{23}^α and F_{23}^β are different. But the term $(F_{23}^\beta - F_{23}^\alpha) \sigma_{32}$ vanishes due to $\sigma_{32} = 0$, resulting in $W_m \equiv 0$.

Generalizing this example, it can be stated that the grains remain thermodynamically identical during a variation of state of the system when:

(i) The differences $(U^\beta - U^\alpha)$, $(S^\beta - S^\alpha)$, $(N_k^\beta - N_k^\alpha)$, $(n_l^\beta - n_l^\alpha)$ and $(V^\beta - V^\alpha)$ remain zero for all grain regions with $N^\beta = N^\alpha$;

(ii) The work W_m of the transformation of one grain to the other, given by Eq. (31), remains identically zero.

The term in W_m with $i = 3$ equals $(V^\beta - V^\alpha) \sigma_{33}$ and thus vanishes. As a result, the condition $W_m \equiv 0$ reduces to the identity

$$\sum_{i=1,2} F_{11} F_{22} V' (F_{i3}^\beta - F_{i3}^\alpha) \sigma_{3i} \equiv 0. \quad (90)$$

As discussed in Section III C, the left-hand side of this expression is the work of the shear stress along the transformation vector \mathbf{t} projected on the interface plane. This identity is satisfied term by term when the components F_{i3} are equal ($F_{i3}^\beta \equiv F_{i3}^\alpha$) for the directions i in which the stress component σ_{3i} is nonzero. In fact, Eq. (90) reduces to this case after an appropriate rotation of the coordinate axes. Note that coupled GBs²⁴ can be equilibrated under stress as long as the relevant component of σ_{3i} is zero.

Under the above conditions, the phase-change equilibrium equation (30) is satisfied as an identity. Furthermore, it can be shown that when conditions (i) and (ii) are satisfied, Eqs. (45) and (46) become identical to each other and only one of them should be solved simultaneously with Eq. (41). As a result, γA is obtained by solving a system of only two equations, giving

$$\gamma A = [U]_X - T[S]_X - \sum_{k=2}^K M_{k1} [N_k]_X - \phi_1 [N]_X - \sum_{l=1}^L \mu_l [n_l]_X - \sum_{i=1,2,3} [V \bar{F}_{i3} / \bar{F}_{33}]_X \sigma_{3i}, \quad (91)$$

where

$$[Z]_X := \frac{\begin{vmatrix} Z & X \\ Z^\alpha & X^\alpha \end{vmatrix}}{X^\alpha} = Z - Z^\alpha X / X^\alpha. \quad (92)$$

Index α refers to one of the grains. By specifying X , one term in Eq. (91) is eliminated. The coefficients $[V\bar{F}_{i3}/\bar{F}_{33}]_X$ are the excess shears ($i = 1$ or 2) and excess volume $[V]_X$ ($i = 3$) of the GB.

Similarly, if conditions (i) and (ii) are satisfied, then the Gibbs-Duhem equations (33) and (34) for the grains become identical to each other and the adsorption equation is obtained by solving a system of only two equations:

$$\begin{aligned} d(\gamma A) = & -[S]_X dT - \sum_{k=2}^K [N_k]_X dM_{k1} - [N]_X d\phi_1 - \sum_{l=1}^L [n_l]_X d\mu_l \\ & - \sum_{i=1,2,3} [V\bar{F}_{i3}/\bar{F}_{33}]_X d\sigma_{3i} + \sum_{i,j=1,2} \tau_{ij}^X A de_{ji}. \end{aligned} \quad (93)$$

Again, one variable in Eq. (93) is eliminated by specifying the extensive property X , which reduces the number of independent differentials to $(K + L + 6)$. The actual number of independent variations is less due to the symmetry-related constraints imposed for preservation of the identity of the grains. In the absence of shear stresses, the last but one term in Eq. (93) reduces to $[V]_X d\sigma_{33}$. In this particular case, Eq. (93) can be applied to both coherent and incoherent symmetrical tilt boundaries. We emphasize again that for Eqs. (91) and (93) to be valid, the condition $F_{i3}^\beta = F_{i3}^\alpha$ must be satisfied for the directions i in which $\sigma_{3i} \neq 0$.

The last term in Eq. (93) contains the GB stress τ_{ij}^X . Assuming that grain α is the reference state of strain, it is straightforward to derive

$$\begin{aligned} \tau_{ij}^X &= \frac{1}{A} [V'\bar{Q}_{ij}]_X \\ &= \frac{1}{A} \left(\bar{\sigma}_{ij} V - \delta_{ij} \sigma_{33} V - AB_i \sigma_{3j} - \delta_{ij} \sum_{k=1,2} AB_k \sigma_{3k} \right) \\ &\quad - \frac{X}{AX^\alpha} (\sigma_{ij}^\alpha V^\alpha - \delta_{ij} \sigma_{33} V^\alpha), \quad i, j = 1, 2. \end{aligned} \quad (94)$$

Here, V is the bicrystal volume, B is the displacement vector of the upper boundary of the bicrystal during the GB formation [cf. Fig. 3(d)], $\bar{\sigma}_{ij}$ is the volume-averaged stress tensor in the bicrystal, and all quantities with superscript α refer to an arbitrarily chosen homogeneous region of grain α . In the particular case when $X = N$ we have

$$\begin{aligned} \tau_{ij}^N &= \frac{1}{A} \left(\bar{\sigma}_{ij} V - \delta_{ij} \sigma_{33} V - AB_i \sigma_{3j} - \delta_{ij} \sum_{k=1,2} AB_k \sigma_{3k} \right) \\ &\quad - \frac{N}{AN^\alpha} (\sigma_{ij}^\alpha V^\alpha - \delta_{ij} \sigma_{33} V^\alpha), \quad i, j = 1, 2. \end{aligned} \quad (95)$$

For this choice of X , expression (91) for γA takes the form

$$\begin{aligned} \gamma A = & [U]_N - T[S]_N - \sum_{k=2}^K M_{k1}[N_k]_N - \sum_{l=1}^L \mu_l[n_l]_N \\ & - \sigma_{33}[V]_N - A \sum_{i=1,2} B_i \sigma_{3i}. \end{aligned} \quad (96)$$

Eqs. (95) and (96) will be used in Part II of this work.²⁵

VI. DISCUSSION AND CONCLUSIONS

We developed a thermodynamic theory of coherent solid-solid interfaces in multicomponent systems under a general non-hydrostatic state of stress. All equations were derived directly from the First and Second Laws of thermodynamics. No Hooke's law or any other constitutive laws of elastic deformation were invoked. No assumptions were made regarding the interface structure other than the conservation of sites and elastic response to applied shear stresses.

To circumvent the problem of undefined chemical potentials of substitutional components, we treat such components separately from interstitial components using diffusion potentials introduced by Larchè and Cahn.^{13–15} Diffusion potentials in non-hydrostatic solids are well-defined quantities and, similar to chemical potentials, are uniform throughout an equilibrium system. Because a system containing K substitutional components has only $(K - 1)$ diffusion potentials [see Eq. (9)], the requirement of their equality in coexisting phases ($M_{k1}^\alpha = M_{k1}^\beta$, $k = 2, \dots, K$) must be augmented by one more condition, namely, the phase-change equilibrium equation discussed in Sections III B and III C.

As an alternative to diffusion potentials, one can formulate the equilibrium conditions in terms of the ϕ -potentials introduced in this work [Eq. (18)]. Equilibrium with respect to substitutional components is then expressed by K relations $\phi_k^\alpha = \phi_k^\beta$ ($k = 1, \dots, K$), which subsume the phase-change equilibrium condition. Written in terms of the ϕ -potentials, many equations of phase equilibrium and interface thermodynamics look similar to the familiar equations for fluid systems,³ with the ϕ -potentials playing the role of chemical potentials. In the particular case of hydrostatically stressed solids, the ϕ -potentials coincide with real chemical potentials, which are well-defined thermodynamic quantities under hydrostatic conditions. It should be emphasized, however, that the ϕ -potentials do not solve the problem of undefined chemical potentials in non-hydrostatic solids in general. If we choose a different interface plane between the same two phases,

the ϕ -potentials will need to be redefined and will generally take on different numerical values.

An important result of this paper is the coherent phase coexistence equation derived in Section III D. It can be written as

$$0 = -\{S\}_X dT - \sum_{k=1}^K \{N_k\}_X d\phi_k - \sum_{l=1}^L \{n_l\}_X d\mu_l - \sum_{i=1,2,3} \{V F_{i3}/F_{33}\}_X d\sigma_{3i} + \sum_{i,j=1,2} \{V' Q_{ij}\}_X dF_{ji} \quad (97)$$

and is a generalization of the Clapeyron-Clausius equation to non-hydrostatically stressed multicomponent systems. In the particular case when the phases are hydrostatic, we have $Q_{ij} = 0$, $\phi_k = \mu_k$, and this equation reduces to

$$0 = -\{S\}_X dT - \sum_{k=1}^{K+L} \{N_k\}_X d\mu_k + \{V\}_X dp, \quad (98)$$

where we use the same symbol N_k for the amounts of substitutional and interstitial components. For single-component phases this equation recovers the classical Clapeyron-Clausius equation $0 = -\{S\}_{N_1} dT + \{V\}_{N_1} dp$.²¹ Eq. (97) predicts a rich variety of relations between temperature, stress and chemical compositions of coexisting phases, which call for testing by experiments and simulations in the future.

Hydrostatic phase coexistence conditions and the Clapeyron-Clausius equation have been extensively tested by experiment and simulations. The conditions of coherent equilibrium between non-hydrostatic phases^{12–14} (Section III B) and the phase coexistence equation (97) derived in this work call for a similar verification. An analogue of Eq. (97) for solid-fluid systems has been recently tested by atomistic simulations which implemented strongly non-hydrostatic conditions in the solid.^{9,10} A similar analysis and simulations could be performed for solid-solid interfaces. In particular, it should be possible to test Eq. (37) by studying the relation between variations in the diffusion potential and the shear stress.

We defined the interface free energy γA as the reversible non-mechanical work performed in a thought experiment in which the interface was formed by transforming a part of a single-phase system into a different phase. We have shown that γA can be expressed as excesses of different thermodynamic potentials, depending on the choice of the reference properties X and Y in Eq. (48). Two examples of such potentials are given by Eqs. (52) and (53).

Despite the freedom of choice in expressing γA as an excess, it still remains the work of interface formation and therefore must be unique. The following comment is due in this connection.

The last sum in Eqs. (47) and (48) is the mechanical work performed by the applied stress during the phase transformation. This work depends on the transformation strain, which we assumed to be known. However, crystal symmetry may lead to multiplicity of possible transformation paths between the same two phases. In other words, given the same reference state there can be different deformation gradients \mathbf{F}^α and \mathbf{F}^β producing exactly the same physical states of the phases. Some of such alternate transformation paths can actually be implemented in experiments or atomistic simulations. The situation is similar to the existence of symmetry-dictated multiple modes of coupled GB motion. Depending on the temperature and other factors, a moving GB can produce different shear deformations of the receding grain, each corresponding to a different mode of coupling. The existence of multiple coupling modes was confirmed by both simulations^{24,26–28} and experiments^{29–32} on symmetrical tilt grain boundaries.

The multiplicity of possible transformation strains seems to create the following paradox: given a two-phase system in its current state, how does one know which of the transformation strains should be plugged in Eq. (48) to obtain the correct value of γA ? The answer lies in the fact that the phase equilibrium equation (35) also depends on the transformation strain through the coefficients in front of $d\sigma_{3i}$. As discussed in Section III C, one of the equilibrium conditions is the neutrality with respect to spontaneous interface displacements in an open system. The actual deformations of the phases occurring during such displacements determine the equilibrium states of the phases. Different deformation gradients will lead to different equilibrium states. The equilibrium states of the phases, in turn, affect the interface free energy and all other interface properties. If the actual transformation strain realized in a given experiment or simulation changes, so will the equilibrium states of the phases and thus γA . Thus, knowing the current state of the two-phase system, one should be able to tell which of the symmetrically possible strains is actual and thus correctly predict the interface properties.

Larchè and Cahn^{13–15} realized that thermodynamic equilibrium between solid phases depends on the degree of coherency of the interface. The above discussion suggests that, for a coherent interface, the equilibrium also depends on the particular coherent transformation strain (out of several possible by crystal symmetry) which is realized during the interface displacements. So do all thermodynamic properties of the interface. Mathematically, the hypersurface of phase coexistence in the parameter space can have multiple sheets corresponding to different transformation strains between the same two phases. Switches between the transformation strains can cause abrupt changes in states of the phases and thus in interface properties, and are similar to interface

phase transformations. The strain multiplicity and its consequences for interface thermodynamics are worth exploration in future work. One way to do so would be to use Eq. (37) and apply the stress in different directions which activate different transformation paths.

The generalized adsorption equation derived in this paper expresses the differential of the interface free energy in terms of a set of independent intensive parameters characterizing the equilibrium state of a coherent two-phase system. Different forms of this equation are given by Eqs. (58), (59), (60), (65), (66) and (70). The adsorption equation can be considered as the differential form of the fundamental equation of the interface, whereas Eq. (48) the fundamental equation is a functional form. The differential coefficients in the adsorption equation define those interface excesses which are measurable physical quantities. In particular, the interface stress tensor τ emerges from the coefficients in front of the lateral strains e_{ij} and is formally defined by Eq. (61). It should be emphasized that the excess formulation of the interface stress presented in this work is not as trivial as for hydrostatic systems. In the latter case, the lateral stresses in the phases are equal and their interface excess is unique. In non-hydrostatic systems, the lateral stresses in the phases are different and their excess, if calculated relative to a dividing surface, depends on its placement. In terms of Cahn's generalized excesses,⁶ τ depends on the choice of the reference properties X and Y . In this sense, the interface stress between two non-hydrostatically stressed solids is not unique.

To understand the origin of this non-uniqueness, it is instructive to consider its Lagrangian formulation (63). As indicated by Eq. (64), τ_L is the response of the interface free energy γ_L (per unit reference area) to elastic deformations of the interface. Such deformations must be implemented in such a way that to preserve the phase equilibrium. In other words, the derivative in Eq. (64) must be taken along a certain direction on the phase coexistence hypersurface in the parameter space. Derivates taken along different directions give generally different values of the interface stress, resulting in its multiplicity. The direction in which we take the derivative is controlled by the choice of the reference properties X and Y .

Another excess quantity appearing in the generalized adsorption equation is the interface excess shear. It characterizes the local elastic shear deformation of the interface region in response to a shear stress applied parallel to the interface. The excess shears $[V\bar{F}_{13}/\bar{F}_{33}]_{XY}$ and $[V\bar{F}_{23}/\bar{F}_{33}]_{XY}$ are conjugate to the shear stress components σ_{31} and σ_{32} , respectively. Clearly, the excess shears are specific to coherent interfaces and are undefined for interfaces that do not support shear stresses. This explains why they did not appear in previous versions of the adsorption equation existing in the literature. For practical purposes, the excess shears can be normalized by the physical

or Lagrangian interface area, giving the specific shears $[V\overline{F}_{i3}/\overline{F}_{33}]_{XY}/A$ and $[V\overline{F}_{i3}/\overline{F}_{33}]_{XY}/A'$, respectively. These quantities are similar to the GB “slip” introduced in the context of the effective elastic response of GBs in polycrystalline materials.³³ Excess shears of individual GBs in copper calculated by atomistic methods will be reported in Part II of this work.²⁵

The analysis presented in this work is limited to a plane interface between semi-infinite homogeneous phases. In the future, some of these constraints could be lifted by including, for example, the effect of curvature or inhomogeneity. Such generalizations appear to be extremely challenging but could benefit from the ideas and methods developed previously in the mechanical theories of interfaces.^{16–18} As already mentioned, the mechanical theories consider only mechanical equilibrium between the phases and do not impose the conditions of chemical or phase equilibrium. They consider deformations of an *already existing* interface and disregard the process of its *formation*, which, as we saw above and will see again in Part II,²⁵ can be accompanied by finite transformation strains. This prevents the mechanical approach from properly defining γ and deriving the adsorption equation. Nevertheless, various interface excess stresses and strains were identified, and carefully described mathematically, under much more general conditions than in the present work. Besides the excess shear and excess volume considered here, the mechanical analysis reveals a few other excess strains arising, for example, when the phases are curved and/or capable of relative rotation and/or tilt.¹⁷

Finally, we note that our analysis neglects the existence of vacancies, which is justified by their small concentration in most solids. In the absence of vacancy sources and sinks in the system, the total number of vacancies is conserved and they could be included in our analysis as simply one of the substitutional components. In this case, the number of vacancies could be treated as one of the independent parameters alongside the amounts of real substitutional components. As an alternate model, the vacancies can be assumed to be in equilibrium with some sources and sinks existing far away from the interface. In this case, the number of vacancies in any reference region of the system is a *dependent* parameter, whose value can be determined from the condition of equilibrium with the sources and sinks. It should be noted, however, that the vacancy equilibrium depends on specific properties of the sources and sinks. For example, one can assume that the phases terminate at surfaces parallel to the interface. Suppose the surfaces are in contact with an inert atmosphere exerting a pressure p and are capable of absorbing and creating vacancies. The number of vacancies in such a system is readily predictable and depends on p (Ref. 34). However, the shear stresses σ_{31} and σ_{32} have to be zero because of the presence of surfaces. Thus, this model

will not capture the interesting interface properties associated with the shear stresses.

On the other hand, a uniform distribution of vacancy sources and sinks inside the phases, e.g. in the form of climbing dislocations, would require a radical revision of the underlying assumptions of the present analysis, particularly regarding the conservation of sites. This would also raise the questions of possible creep deformation of the stressed phases and the legitimacy of using the reference state formalism for the description of elastic deformations. In view of these complications, analysis of the possibility of incorporation of equilibrium vacancies in thermodynamics of coherent interfaces is left for future work.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, the Physical Behavior of Materials Program, under Grant No. DE-FG02-01ER45871.

* Electronic address: tfrolov@gmu.edu

† Electronic address: ymishin@gmu.edu

- ¹ A. P. Sutton and R. W. Balluffi, *Interfaces in Crystalline Materials*, Clarendon Press, Oxford, 1995.
- ² Y. Mishin, M. Asta, and J. Li, *Acta Mater.* **58**, 1117 (2010).
- ³ J. W. Gibbs, *The collected works of J. W. Gibbs*, volume 1, Yale University Press, New Haven, 1948.
- ⁴ R. Shuttleworth, *Proc. Phys. Soc.* **63**, 444 (1949).
- ⁵ R. C. Cammarata, Generalized thermodynamics of surfaces with applications to small solid systems, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen, volume 61, pages 1–75, Elsevier Academic Press, 2009.
- ⁶ J. W. Cahn, Thermodynamics of solid and fluid surfaces, in *Interface Segregation*, edited by W. C. Johnson and J. M. Blackely, chapter 1, pages 3–23, American Society of Metals, Metals Park, OH, 1979.
- ⁷ T. Frolov and Y. Mishin, *Phys. Rev. B* **79**, 045430 (2009).
- ⁸ T. Frolov and Y. Mishin, *J. Chem. Phys.* **131**, 054702 (2009).
- ⁹ T. Frolov and Y. Mishin, *Phys. Rev. B* **82**, 174113 (2010).
- ¹⁰ T. Frolov and Y. Mishin, *Phys. Rev. B* **82**, 174114 (2010).

- ¹¹ T. Frolov and Y. Mishin, *Model. Simul. Mater. Sci. Eng.* **18**, 074003 (2010).
- ¹² P. Y. F. Robin, *American Mineralogist* **59**, 1286 (1974).
- ¹³ F. Larchè and J. W. Cahn, *Acta Metall.* **21**, 1051 (1973).
- ¹⁴ F. C. Larchè and J. W. Cahn, *Acta Metall.* **26**, 1579 (1978).
- ¹⁵ F. C. Larchè and J. W. Cahn, *Acta Metall.* **33**, 331 (1985).
- ¹⁶ M. E. Gurtin and A. I. Murdoch, *Arch. Rat. Mech. Anal.* **57**, 291 (1975).
- ¹⁷ M. E. Gurtin, J. Weissmuller, and F. Larchè, *Philos. Mag. A* **78**, 1093 (1998).
- ¹⁸ E. Fried and M. E. Gurtin, *J. Statist. Phys.* **95**, 1361 (1999).
- ¹⁹ L. E. Malvern, editor, *Introduction To The Mechanics Of A Continuous Medium*, Prentice-Hall, Upper Saddle River, 1969.
- ²⁰ P. W. Voorhees and W. C. Johnson, The thermodynamics of elastically stresses crystals, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen, volume 59, pages 2–201, Elsevier Academic Press, 2004.
- ²¹ L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I*, volume 5 of *Course of Theoretical Physics*, Butterworth-Heinemann, Oxford, third edition, 2000.
- ²² J. Q. Broughton and G. H. Gilmer, *Phys. Rev. Lett.* **56**, 2692 (1986).
- ²³ P. L. Williams and Y. Mishin, *Acta Mater.* **57**, 3786 (2009).
- ²⁴ J. W. Cahn, Y. Mishin, and A. Suzuki, *Acta Mater.* **54**, 4953 (2006).
- ²⁵ T. Frolov and Y. Mishin, submitted as Part II of this work, 2012.
- ²⁶ J. W. Cahn, Y. Mishin, and A. Suzuki, *Philos. Mag.* **86**, 3965 (2006).
- ²⁷ Y. Mishin, A. Suzuki, B. Uberuaga, and A. F. Voter, *Phys. Rev. B* **75**, 224101 (2006).
- ²⁸ A. Suzuki and Y. Mishin, *Mater. Sci. Forum* **502**, 157 (2005).
- ²⁹ T. Gorkaya, D. A. Molodov, and G. Gottstein, *Acta Mater.* **57**, 5396 (2009).
- ³⁰ T. Gorkaya, K. D. Molodov, D. A. Molodov, and G. Gottstein, *Acta Mater.* **59**, 5674 (2011).
- ³¹ D. A. Molodov, T. Gorkaya, and G. Gottstein, *Scripta Mater.* **65**, 990 (2011).
- ³² D. A. Molodov, T. Gorkaya, and G. Gottstein, *J. Mater. Sci.* **46**, 4318 (2011).
- ³³ J. Weissmüller, J. Markmann, M. Greuer, and R. Birringer, *Acta Mater.* **59**, 4366 (2011).
- ³⁴ C. J. Herring, *J. Appl. Phys.* **21**, 437 (1950).
- ³⁵ For brevity we will be referring to the particles forming the solid as atoms, although they can also be molecules as in the case of molecular solids.
- ³⁶ Some solids contain atoms capable of occupying both substitutional and interstitial positions. This case

is not discussed here but it is straightforward to generalize our analysis to such solids.

- ³⁷ In their analysis of coherent equilibrium, Larchè and Cahn^{13,14} used the first Piola-Kirchoff tensor which is the transpose of the tensor used in our work.
- ³⁸ Out of this set of $(K + L + 6)$ parameters, only $(K + L + 5)$ are independent (see Section III D). To maintain the neutral two-phase equilibrium, only $(K + L + 5)$ independent variables must be fixed, which automatically fixes the remaining parameter.
- ³⁹ See Section VI for a discussion of possible non-uniqueness of the transformation strain and thus vector \mathbf{t} .
- ⁴⁰ It will suffice to fix only $(K + L + 5)$ of these $(K + L + 6)$ parameters. The remaining parameter is dependent and will be fixed automatically.
- ⁴¹ Because the two-phase region has the same cross-section at every height, its volume equals the volume of the parallelepiped formed by its vertices, see Fig. 3(e). The volume of this parallelepiped is $F_{11}F_{22}\overline{F}_{33}V'$.
- ⁴² By contrast, the shear stress σ_{32} applied normal to the tilt axis destroys the identity of the grains. This stress causes coupled GB motion,²⁴ which cannot be prevented unless we create different chemical compositions in the grains and thus a thermodynamic driving force balancing the driving force of coupled motion. But then the grains essentially become two different phases.

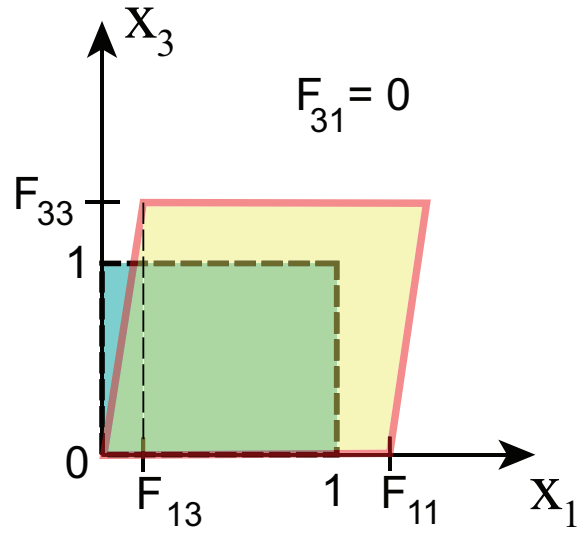


Figure 1: Two-dimensional schematic of a volume element undergoing a finite deformation. In the reference state (dashed lines), the volume element is a unit square. The components of the deformation gradient \mathbf{F} correspond to the new lengths and projections of the edges of the reference square in the deformed state (solid lines).

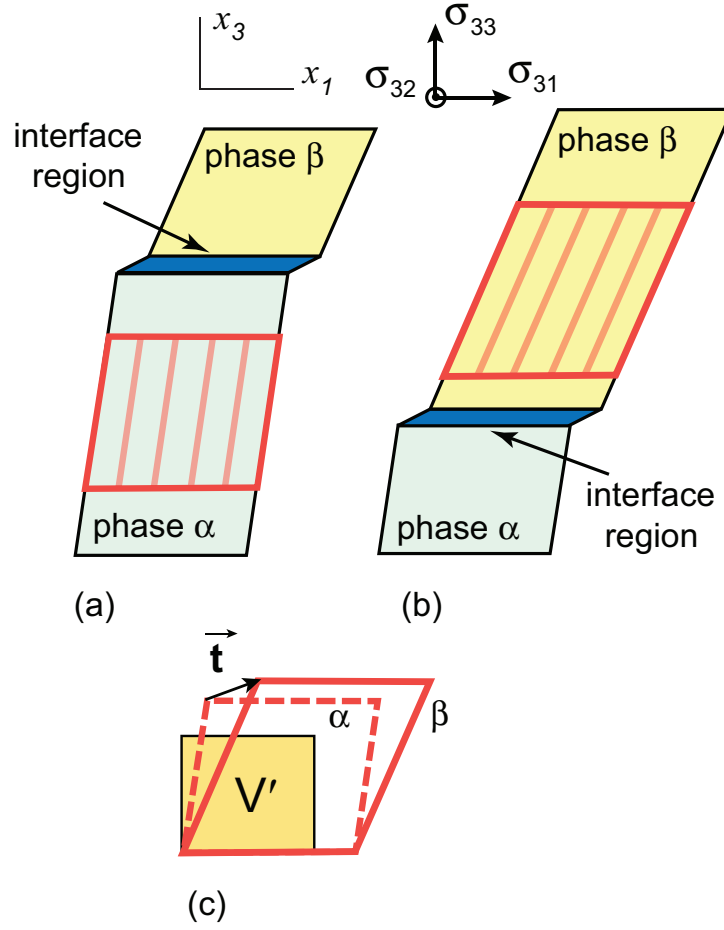


Figure 2: Two-dimensional schematic of phases α and β separated by a coherent interface. When the interface moves down, the striped region of phase α shown in (a) transforms the striped region of phase β shown in (b). In (c), the reference volume element V' (shaded unit square) transforms to the coherent phases α (dashed lines) and β (solid lines). The differences between the deformation-gradient components F_{13} and F_{33} in the phases form the transformation vector \vec{t} .

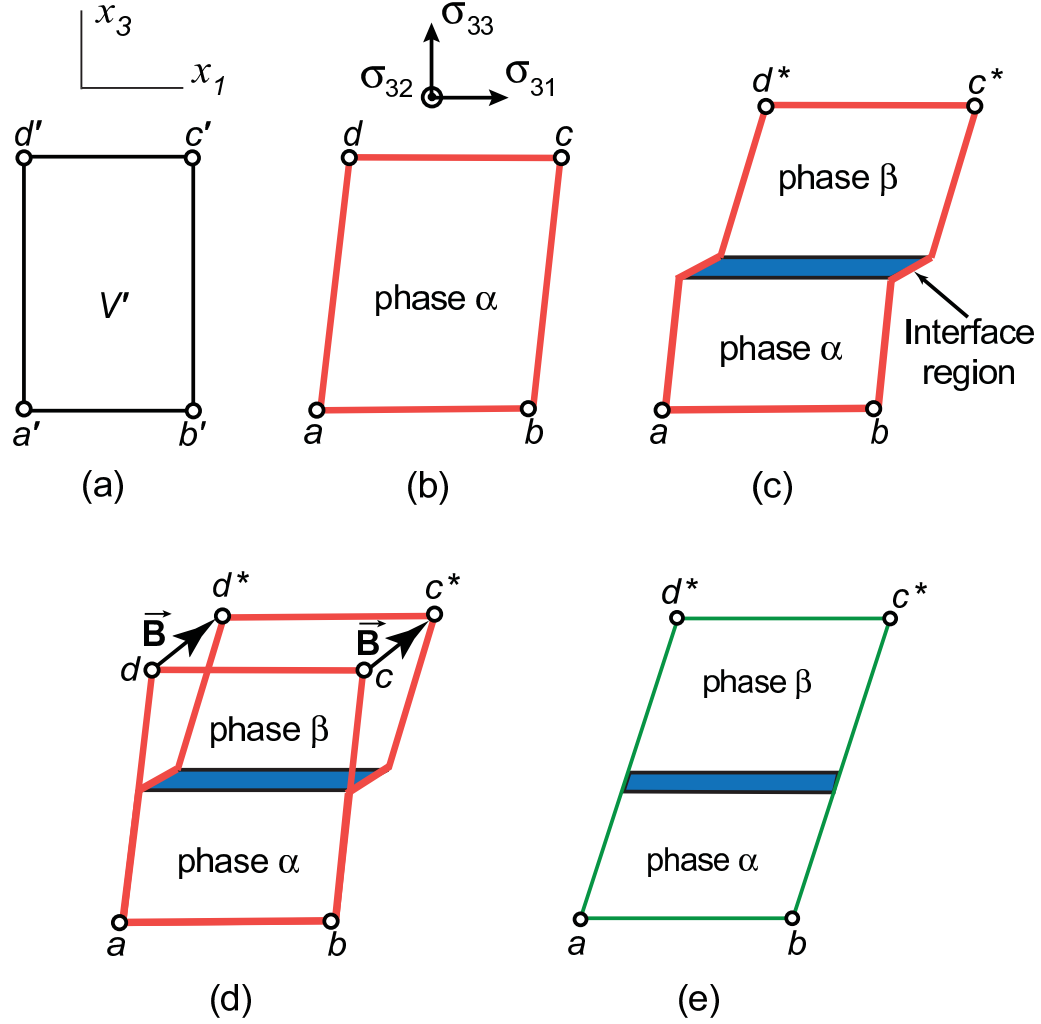


Figure 3: Two-dimensional schematic of coherent transformation of a region of phase α to a two-phase region containing phases α and β separated by an interface. (a) Reference state of the region. (b) Deformed phase α . (c) Two-phase region. (d) Overlapping shapes of phase α and the two-phase region, showing the displacement vector \vec{B} . The open circles mark selected physical points labeled a through d with the prime indicating the reference state and the asterisk indicating the two-phase state. The parallelogram defined by the vertices a , b , c^* and d^* is shown separately in (e).

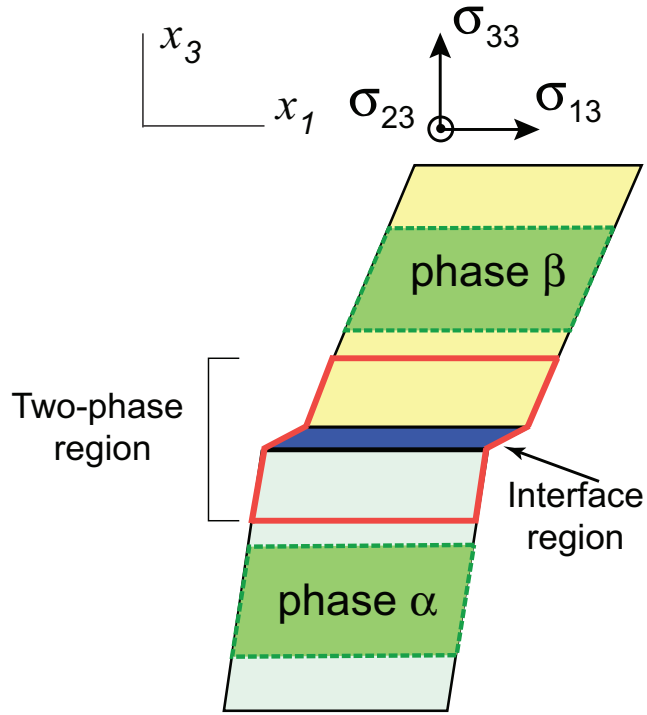


Figure 4: The two-phase region used in the derivation of expressions for the total interface free energy γA . The single-phase regions used in the derivation are chosen outside the two-phase region.